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Yttria stabilised zirconia (YSZ) membranes and their applications

By

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Abstract

The development of ceramic hollow-fibre membranes has gradually grown in the past decade. This specific geometry which has a high surface area per unit volume can dramatically increase the efficiency of separation processes and can be adapted to a variety of industrial applications. In addition, ceramic membranes are well known for their superior chemical and thermal stability which allows them to operate at high temperatures and/or in chemically harsh environments. Nevertheless, the main challenge for their industrial application is their insufficient mechanical strength.

Yttria-stabilized zirconia (YSZ) is selected as a membrane material in this study. This is because the material has superior mechanical strength and it is relatively cheaper than other ceramic materials. The ionic conducting property of YSZ material is also a benefit when it is used in electrochemical applications.

Porous and dense YSZ hollow-fibre membranes have been developed in the study using a combined phase inversion and sintering process. Different membrane morphologies, surface properties, mechanical strength and porosity could be achieved by controlling the YSZ content and sintering temperature. The developed YSZ hollow-fibre membranes with porous or dense structures show great potential for a variety of applications.

Porous YSZ hollow-fibre membranes can be used as membrane contactors in aqueous media or for fluid separations in harsh environments, which most polymeric membranes cannot withstand. For the application of membrane contactors in aqueous media, the nature of the YSZ membranes must be modified from hydrophilic to hydrophobic in order to keep them non-wetted during the aqueous contacting processes.

A robust and hydrophobic YSZ hollow-fibre membrane was developed by introducing a pretreatment technique, followed by a grafting procedure. The hydrophobic YSZ membrane was found to be thermally stable up to 270 °C and chemically stable in hexane for 100 h. This membrane was then applied to the absorption of carbon dioxide from a high concentration aqueous ethanolamine solution. The results

demonstrated the high efficiency of the ceramic hollow-fibre membrane contactor compared to traditional devices.

Dense YSZ hollow-fibre membranes with outer diameters of 1.28 mm have been used as an electrolyte support in a solid oxide fuel cell. The YSZ electrolyte-supported SOFC was prepared at relatively lower sintering temperatures and shorter sintering durations. The YSZ-based hollow fibre SOFC demonstrated its ionic stability in a redox environment and mechanical stability at temperatures up to 800 °C. The results also demonstrated its electrochemical performance at high temperature.

In summary, this thesis focuses on the development of YSZ hollow-fibre membranes from the initial step of fabricating the membrane to the final step of their potential application. Different structures of YSZ hollow-fibre membranes were studied, discussed and their potential performance was compared to the achievements of others in order to gain more understanding and information on the use of the membranes for practical applications.

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Chapter 1 Introduction

1.1 Background

The surge of interest in membrane technology began in the late 1960s. [1] Membrane technology shows many advantages over traditional separation technologies such as distillation and extraction, including higher selectivities, faster separation rates, energy and cost savings, easier and cheaper preparation, smaller size etc. Therefore, the technology has been extensively used in many chemical sectors and in a broad range of applications, for example in reverse osmosis, gas separation and filtration, hemodialysis, electrodialysis, drug delivery etc. [1, 2]

A membrane can be considered as a selective barrier which has the ability to control the permeation of a chemical species through the membrane. The main objective of the process is to allow only one component of a mixture to permeate through the membrane, while blocking the permeation of other components. A membrane may also control the permeation rate of a chemical species through the membrane. For illustration, in controlled drug delivery, the aim is to control the permeation rate from a drug reservoir to the body.

Most membrane processes are performed using polymeric membranes which operate ineffectively in high temperature and chemically harsh environments. Therefore, these processes are limited to operating at low temperature and in moderate conditions.

Ceramic materials are well known for their superior thermal and chemical stability and therefore they have great potential for application in membrane technology. Using a newly developed combined phase inversion and sintering process, ceramic membranes can be produced with hollow fibre geometry which has a much higher surface area unit volume than other geometries such as flat sheet or tubular.

The mechanism of phase inversion in ceramic hollow fibre fabrication is considerably more complex compared to that in polymeric hollow fibre fabrication. A typical phase inversion in a polymeric system involves the interaction of three components:

polymer, solvent and non-solvent. In general, the polymer is dissolved in a solvent to form a homogeneous polymer solution. After immersing the polymer solution into a non-solvent bath, the solvent diffuses out of the polymer solution while the non-solvent diffuses into the solution. The exchange of solvent and non-solvent results in solidification of the polymer solution and the formation of a polymeric membrane. The exchange rate plays an important role in the membrane morphology and different exchange rates can cause varied membrane structures. However, in a suspension system containing ceramic particles and polymer binders, the mechanism of solidification may be different.

The exchange in the ceramic suspension does not only involve solvent and non-solvent, but also involves the movement of ceramic particles. Therefore, the mechanism of the solidification of the ceramic suspension may be more complex. It is important to gain more knowledge and understanding of the solidification process in order to precisely control the morphology and structure of ceramic hollow-fibre membranes.

Porous ceramic hollow-fibre membranes have been applied in many areas such as gas separation, ultrafiltration, nanofiltration, solvent recovery etc. [3-7] The mechanism of the separation process basically relies on the thickness, pore size, and surface porosity of the membrane. In addition, ceramic membranes can be used as a medium in membrane contactor applications. In this type of application, ceramic membranes are used to directly contact with corrosive chemicals or to operate under high temperature conditions in which most polymeric membranes cannot function. [8, 9] So far, there are still very few porous ceramic hollow-fibre membranes which have been employed in these applications.

The development of dense ceramic hollow-fibre membranes is a fairly new area in membrane technology. Some studies have focused on oxygen delivery as it is more economical when using membranes rather than traditional technologies such as cryogenic distillation. For example, Luyten et al. have prepared a dense $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ (LSCF) hollow-fibre membrane by using the phase inversion and sintering process. [10] Tan et al. have not only successfully fabricated a LSCF hollow-fibre membrane, but have also demonstrated oxygen permeation flux at low

operating temperatures, which has been adopted industrially. [11] Other applications such as pure hydrogen production, partial oxidation of methane for syngas production and hydrogenation reactions have also attracted the interest of researchers. [12-14] However, the application of ceramic hollow-fibre membranes has not been employed in energy generation areas such as solid oxide fuel cells (SOFC).

In this thesis, yttria-stabilized zirconia (YSZ) is selected as a ceramic membrane material, as it is relatively cheap and has superior mechanical strength as well as ionic conducting properties. Two main objectives in this study are to develop asymmetric YSZ hollow-fibre membranes using a single step fabrication method and to explore their potential applications. The entire process of YSZ hollow-fibre membrane development, starting with membrane fabrication through membrane characterization, membrane surface modification, to final membrane applications, is covered in this study. Carbon dioxide absorption and solid oxide fuel cells are two selected examples to demonstrate the ability of YSZ ceramic membranes to be employed in conditions in which polymeric membranes are not able to operate.

1.2 Objectives

- 1) To prepare and characterize asymmetric ceramic hollow-fibre membranes using a single step fabrication process:
 - 1.1) To prepare and characterize ceramic hollow-fibre membranes made from yttria-stabilized zirconia.
 - 1.2) To investigate the effect of the properties of ceramic particles and the fabrication process on membrane morphology
 - 1.3) To preliminarily explore the potential applications of different membrane structures (i.e. porous and dense structures).
- 2) To enhance the hydrophobicities of porous YSZ hollow-fibre membranes for gas-aqueous liquid contacting applications.
 - 2.1) To prepare YSZ membranes with high surface hydrophobicity via an improved surface modification method.

- 2.2) To study the effects of grafting parameters in the improved surface modification process on the membrane surface hydrophobicity, morphology, mechanical strength and pore size distributions.
 - 2.3) To study the stability of the grafted membrane in contact with a liquid absorbent for a long period.
- 3) To study the applicability of the hydrophobic and porous YSZ hollow-fibre membranes used as membrane contactors for carbon dioxide absorption at a higher concentration of absorbent.
- 3.1) To produce hydrophobic ceramic hollow-fibre membrane contactors (CHFMC) and apply them to a CO₂ absorption application.
 - 3.2) To investigate the performance of CHFMC.
 - 3.3) To theoretically predict the mass transfer in the CHFMC.
- 4) To study the applicability of dense YSZ hollow-fibre membranes for solid oxide fuel cell (SOFC) applications.
- 4.1) To prepare a dense YSZ hollow-fibre membrane to be used as an electrolyte support for SOFC.
 - 4.2) To characterize the YSZ electrolyte-support with respect to membrane morphology, gas tightness and mechanical strength.
 - 4.3) To investigate the electrolyte performance of the YSZ electrolyte-supported SOFC.

1.3 Thesis structure and presentation

This thesis consists of seven individual chapters addressing the fabrication of YSZ hollow-fibre membranes and their applications. Each chapter has an abstract to capture the essential findings in the sub-study. A more detailed background investigation is described in the introduction section in order to help readers to follow the logical progression of the thesis as a whole. Figure 1.1 shows the overall structure of the thesis.

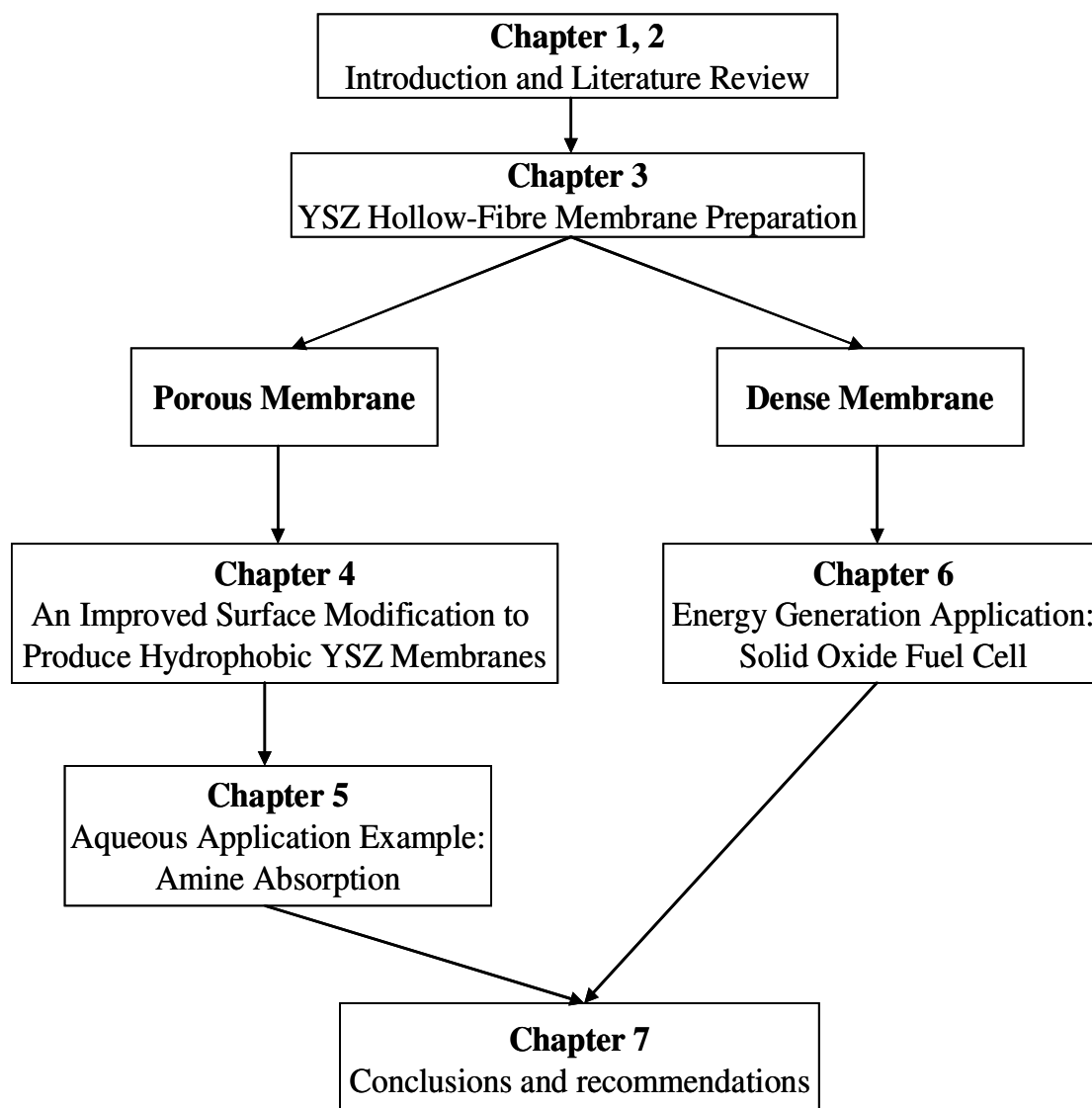


Figure 1.1 The overall structure of the thesis

Chapter 1 describes the basic background of ceramic hollow-fibre membranes and the main objectives of the study. Chapter 2 gives a review of literature regarding the fundamental knowledge of YSZ hollow-fibre membranes and their applications. Chapter 3 focuses on the fabrication and characterization of YSZ hollow-fibre membranes. The effects of the membrane fabrication parameters on membrane properties such as structure, morphology and porosity are covered in this chapter. In chapter 4, the improved surface modification method to enhance the hydrophobicity of porous YSZ hollow-fibre membranes is introduced as well as the characterization of the membrane surface properties. Chapter 5 is dedicated to the application of newly developed hydrophobic YSZ membranes for carbon dioxide-amine absorption. The performance of the YSZ membrane contactor is presented and discussed. In chapter 6,

the new concept of dense YSZ-supported hollow-fibre SOFC is proven. The characterization and electrochemical performance of the SOFC are presented and discussed. Chapter 7 concludes with the general conclusions of the whole study and recommendations for future work.

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Chapter 2 Literature review

2.1 Preparation of yttria stabilized zirconia (YSZ) particles

Most zirconia is extracted from zircon (ZrSiO_4) which occurs in igneous rocks such as granites and pegmatites in Brazil and Madagascar. Zircon can also be found in beach sand in Australia, Brazil, India and Florida. However, the beach sand also contains other materials such as ilmenite, rutile and monazite. The purity of zircon in beach sand is not as high as in igneous rocks. [1]

There are several approaches to produce pure zirconia from zircon. The commercial approach is electric arc melting of zircon at about 1750 °C. At this temperature, zircon can be dissociated into ZrO_2 and SiO_2 . The solid zirconia is produced and coated with liquid silica. After cooling, the solid silica can be washed by boiling sodium hydroxide solution. The residual is washed and the zirconia can be obtained by centrifuging. The purity of the zirconia can reach to about 99%. [2] Another small source of zirconia is from the mineral baddeleyite which is impure monoclinic zirconia and usually contains other minerals such as silica, iron oxide and titania. The mineral baddeleyite can be found in Brazil and South Africa. [1]

Zirconia is widely applied as refractory materials, pigment coatings, and dental materials and some technical uses of zirconia include in barrier coatings, hip joint implants, grinding media, cutting tool and mechanical parts. However, a large volume variation during the cooling process results in a fragmentation of zirconia which restricts the applications of zirconia. [3] To broaden its application, it is necessary to understand the crystallization change mechanism of zirconia. This is needed in order to try to find a way to reduce the volume variation and make zirconia so that it can be used widely.

There are three different crystalline forms in zirconia structure: cubic ZrO_2 , tetragonal ZrO_2 and monoclinic ZrO_2 . Cubic ZrO_2 is the highest temperature form and is stable from 2370 °C to melting point at about 2680 °C. [4] Below 2370 °C, cubic ZrO_2 transforms to the tetragonal ZrO_2 which is thermodynamically stable down to about

1240 °C. Monoclinic ZrO_2 is the lowest temperature form and is stable below 1240 °C. These phase transformations from cubic ZrO_2 to monoclinic ZrO_2 involve not only a change in symmetric structure but also a volume expansion. The volume expansion from cubic ZrO_2 to monoclinic ZrO_2 is about 10%. [5] The phase diagrams of zirconia have been reported by Yashima et al. [6] The volume change causes poor mechanical properties such as cracks and disruptions in structural applications, including reinforced composition and membrane technology. The volume change can be eliminated by lightly doping a few percent of rare earth oxides (stabilizer) such as CaO , MgO , Sc_2O_3 and Y_2O_3 .

The stabilizer can create oxygen vacancy concentration in the crystal structure (i.e. increase the volume for the transformation) of zirconia, allowing it to remain in a metastable form in the whole available temperature range which is normally considered from room temperature to sintering temperature. [3] The volume expansion of stabilized zirconia could be brought down to about 4 %. [7] The reduction of volume change can hence effectively improve the structural stability of zirconia. Due to the structure stability, this stabilized zirconia has been noted and named “ceramic steel” by Garvie et al. [8] Moreover, the additional oxygen vacancies are good charge carriers which can enhance the ionic conductivity of the stabilized zirconia. With these attractive characteristics (i.e. high mechanical strength and good ionic conductivity), studies have drawn more attention to the application of this promising material, partial-stabilized zirconia.

One of the most common applications is as a solid electrolyte. Yttria stabilized zirconia (YSZ) is commonly used as a solid electrolyte material for solid oxide fuel due to its relatively cheaper price, although some stabilizers such as scandia and ytterbia could offer better ionic conductivity. YSZ also exhibits a better mechanical strength than other partial-stabilized zirconia such as $\text{MgO}_2\text{-ZrO}_2$ and $\text{CaO}_2\text{-ZrO}_2$ as shown in Table 2.1. [9] This study has specially focused on YSZ membrane since it has more advantages than other ceramic materials as mentioned above.

Table 2.1 Mechanical property of partial stabilized zirconia

Property	MgO ₂ -ZrO ₂	CaO ₂ -ZrO ₂	Y ₂ O ₃ -ZrO ₂
Wt% stabilizer	2.5-3.6	3.0-4.5	5-10
Bend strength (MPa)	440-720	440-650	650-1000

Hydrothermal synthesis process is the most common technology to make commercial YSZ powder. The crystallite size of the commercial YSZ powder made from Next Tech Material or Tosoh is about 3 to 3000 nm. [10-12] This technology is considered as a chemical synthesis and does not involve a high temperature calcining process which can cause a difficulty to control particle size and increase the cost on those calcination apparatus.

The advantages of hydrothermal synthesis are: (1) the particle size and morphology can be controlled by using different synthesis conditions such as pH value of solution, concentration of reagents, solvent, temperature and pressure; (2) metal oxide can be produced at a low temperature (less than 300 °C) as compared with traditional solid phase reaction and low pressure (less than 15 MPa); (3) the metal oxides are produced by a single step process which can reduce the cost of sintering apparatus and simplify the synthesis process. [10, 12]

In laboratories, YSZ is produced using chemical synthesis. Cubic YSZ powder produced in basic solution has reported by Tsukada et al. [9, 10, 13] They used zirconyl chloride (ZrOCl₂·8H₂O) as the zirconium source and yttrium(III) nitrate pentahydrate (Y(NO₃)₃·5H₂O) as the yttrium source. Y(OH)₃ and Zr(OH)₄ can be coprecipitated from a mixture of ZrOCl₂ and Y(NO₃)₃ by adding basic solution. The resulting dope was heated at different temperatures (from 25 °C to 100 °C), reaction time (from 0.5 hours to 2200 hours) and pH (from 9.5 to 13.9). After being filtered and washed by deionized water, the precipitation of YSZ powder can be obtained.

2.2 Preparation of YSZ membrane

2.2.1 Shaping

Preparation of a ceramic membrane usually involves three steps: (1) generation of a uniform ceramic particle dope which might contain dry powder, water/solvent, binder, additives (lubricant, compaction aid, plasticizer, sintering, surfactant or pore former); (2) packing of the particle dope and shaping the dope into a specific geometry such as flat sheet, monolith, tubular and hollow fibre; (3) consolidation of ceramic particle by a high temperature sintering process which achieves a higher packing density for ceramic particle and offers better mechanical strength for resulting membranes. The resulting packing densities could be different due to the shaping process.

The packing density basically depends on the shaping method as well as the size and distribution of ceramic particles. Theoretically, the optimum packing density of single radius sphere in a two-dimensional (2-D) structure is 70 % (i.e. 30 % porosity remaining) as shown in Figure 2.1. A higher packing density can be achieved to 74 % by filling with a smaller particle. Ideally, the maximum packing density can reach to 77 % in 2-D structure. The particle size for the maximum packing density is in the range between 0.2 μm and 5 mm. [9]

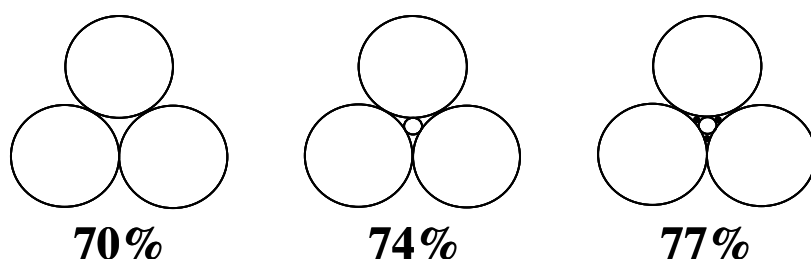


Figure 2.1 Ideally packing density of particle distribution in two-dimensional structure

It can be found that the particle size distribution highly influences the packing density during the shaping process. A high packing density in ceramic dope usually transfers to low porosity on sintered ceramic membrane and further improves the mechanical strength of ceramic membrane.

YSZ membrane can be produced by different kinds of technology such as tape casting, dry press, extrusion and spinning. The details of each technology are described below.

2.2.2 Tape casting

Tape casting is widely used to make a large area and flat YSZ electrolyte-support SOFC. [13-15] The tape casting process is shown in Figure 2.2. [16]

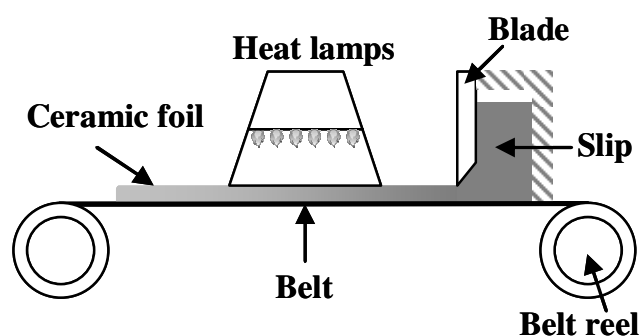


Figure 2.2 Schematic diagram of tape-casting process

The whole facility includes a slip tank, a blade, a flat belt, heat lamps for drying and belt rollers. A feed material of tape casting usually is a free-flowing viscous slip composed of fine ceramic particle (about 50 μm), organic solvent, dispersant, and binder. [9, 13] To form a uniform tape casting membrane, it is important to control the viscosity and homogeneity of the casting slip which is influenced by particle size, particle size distribution, surface area of particle, solvent polarity as well as the ratio between ceramic particle and binder.

Milling is often used to break down agglomerates of powder to produce a homogenous slip. The milled slip is degassed before casting. The slip is spread on the flat belt. The casting thickness can be controlled by the blade gap. The thickness of final dried green tape is approximately half of the blade gap. [17] The thickness of the dried green tape is also influenced by slip viscosity and casting rate. After the casting process, the dried green tape is moved to the drying zone for solvent removal. The drying rate by solvent evaporation is an important parameter which could affect membrane morphology and membrane permeability. The resulting dried green tape is then ready for further processing such as cutting and sintering.

The thickness of YSZ ceramic membrane fabricated by this method is in a range from 5 μm to 200 μm . [18] The mechanical strength of tape casting YSZ ceramic membrane is about 200 MPa. [19]

2.2.3 Dry pressing

Dry pressing is a simple uniaxial pressing process shown in Figure 2.3. The dry pressing is carried out in a die with two movable punches, those are, top punch and bottom punch. Before dry powder is filled into the die, the powder should be well granulated and sieved to reduce the density variation.

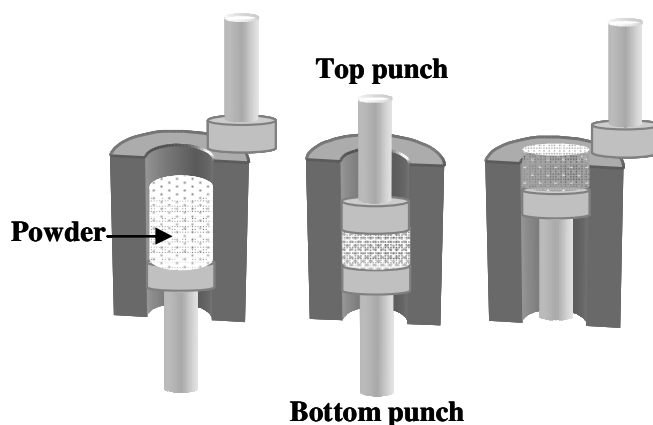


Figure 2.3 Schematic diagram of dry-pressing process

Small and flat ceramic membrane can be produced by the method. Xin et al used the method to prove that a thin and dense electrolyte can be fabricated by using nano-size YSZ particles. [20] In their study, YSZ powder, NiO powder, flour and organic binder were first mixed to homogeneous and pressed under 200 MPa. The resulting green anode support was 13mm in diameter and 0.6mm in thickness. Nano-size YSZ powder was then uniformly pressed on the anode support. A uniaxial pressure of 250 MPa was applied to disrupt the agglomerate of nanopowder and form a thin dense YSZ layer on the anode support. The dual layers of green body, consisting of an anode support and a thin YSZ electrolyte was subsequently sintered at 1400 $^{\circ}\text{C}$ for 4 hours. After cooling, cathode paste consists of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$, YSZ and ethyl cellulose was applied on the YSZ electrolyte and sintered at 1200 $^{\circ}\text{C}$ for 2 hours. A thin electrolyte (about 8 μm) has been successfully prepared using the nano-size YSZ particles. The anode-support SOFC with a thin YSZ electrolyte showed a better

electrochemical performance than other flat-sheet SOFC. Dry pressing membrane is suitable for laboratory-scale testing particularly on pilot or fundamental research.

2.2.4 Extrusion

Extrusion is widely used to fabricate ceramic rods and ceramic tubes. As can be seen from Figure 2.4, the extraction involves forcing a deformable dope solution through a die orifice. The dope is very viscous (i.e. semi-solid mixture, or paste) for extrusion as the extruded precursor must be sufficiently strong to be broken off from the die and moved to a rack for drying without significant twist or distortion.

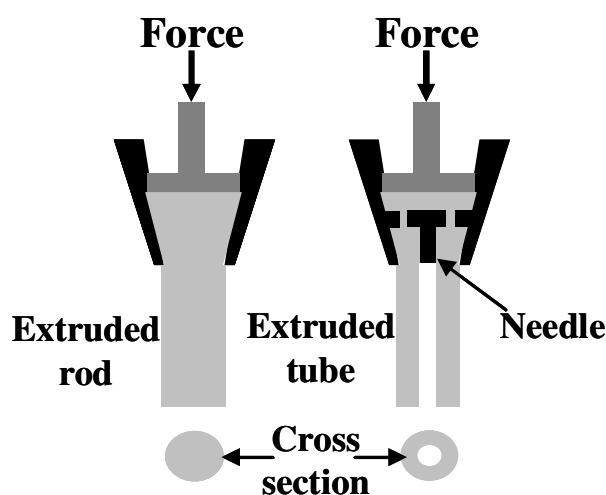


Figure 2.4 Schematic diagram of extrusion process

The viscous dope can be formed by controlling the amount of water, solvent, ceramic powder, binder and additives. A visible shrinkage can be found on drying and a greater shrinkage can be observed after sintering. The optimum parameters of tubular YSZ fabrication, including size of ceramic particle, composition of dope solution, viscosity, extrusion rate, dry condition and sintering conditions have been studied by Du wt al. [21, 22] The outer diameter (o.d.) and inner diameter (i.d.) of the YSZ tube is around 3 and 2.7 mm, respectively.

Commercial YSZ tube with o.d. / i.d. of 5 / 8 mm can be purchased from Nikkato (Japan). They have been widely used as solid electrolytes for gas sensors. [23-29]

Other companies such as Viking Ceramics Limited (Denmark), Coors Ceramics (USA), and Zircoa (USA) also supply YSZ tubes.

Note, a membrane prepared from extrusion has a symmetric structure. In general, a membrane with a symmetric structure shows a better mechanical strength than that with an asymmetric structure. Another advantage of the method is that a large quantity of ceramic material can be extruded in a very short time. Either tubes or rods can be produced rapidly.

2.3 Fabrication of hollow-fibre membrane

Studies have generated considerable interest in ceramic hollow-fibre membrane because of its chemical and thermal stability as well as considerable large surface area per volume. The prior development of ceramic hollow-fibre membrane prepared by a phase inversion/sintering method was applied to gas separation and ultrafiltration in the 1990s. [30] However, the fabrication process of ceramic hollow-fibre membrane was still not clear since the method is quite complex. A clearer and more complete fabricating process has been revealed by Tan et al. and Liu et al. [31, 32] Since then, the phase inversion/sinter method is widely used to prepare ceramic membrane from different materials for different applications. Examples of studies using this method are: De Jong et al. used a triple-orifice spinneret to produce a double-layer alumina hollow-fibre membrane for separation technology; [33] Tan et al. developed a mix-conducting ceramic hollow-fibre membrane for oxygen production; [34] Liu. et al. prepared a $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ hollow-fibre membrane for hydrogen separation at high temperature. [35] Some studies employed YSZ hollow-fibre membrane as a solid electrolyte for SOFC. [36, 37]

The typical phase inversion/sintering method included three steps: the preparation of spinning dope, the spinning of ceramic membrane precursor and final sintering. Figure 2.5 demonstrates the relationship between operating parameters and resulting effects in each step for the method. The details of each step are discussed below.

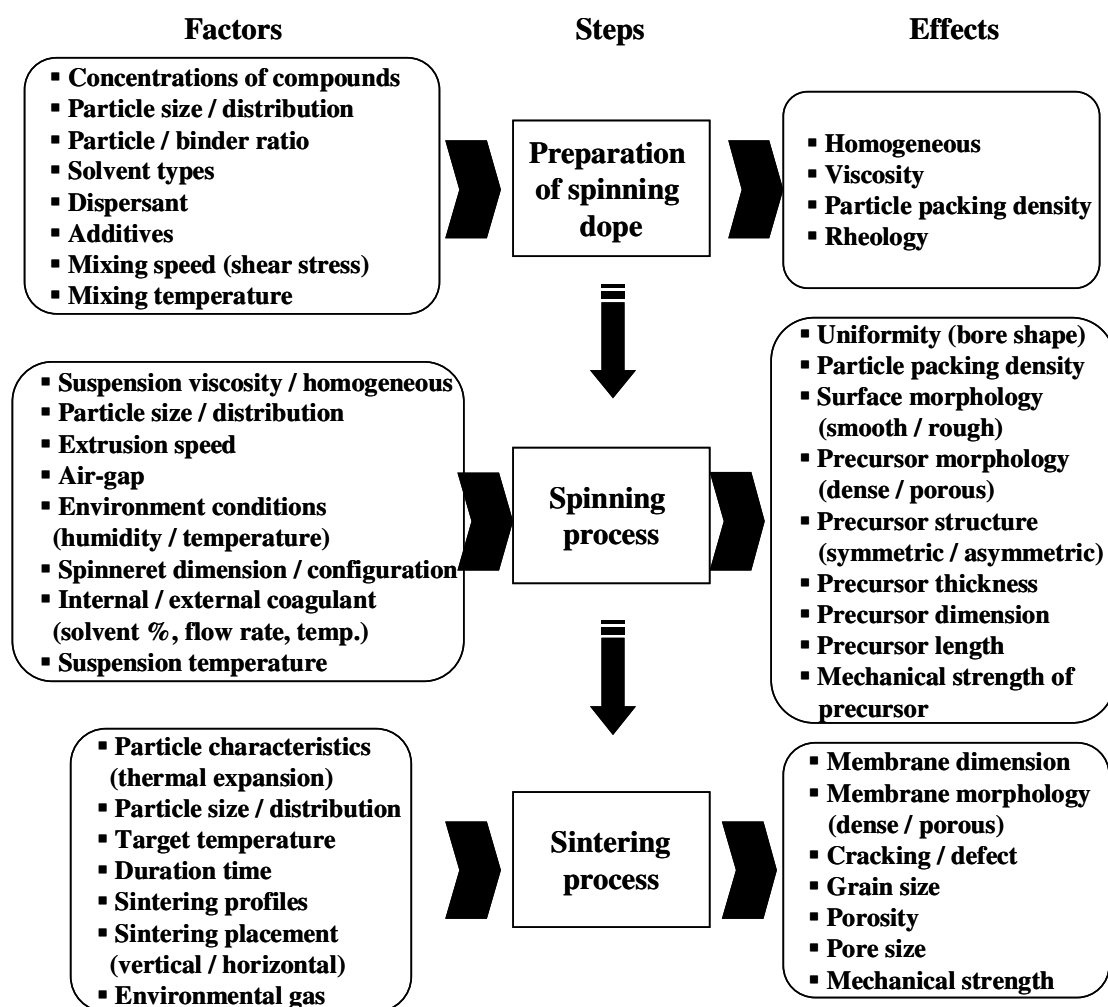


Figure 2.5 Flow chart of spinning process

2.3.1 Preparation of spinning dope

A spinning dope is a viscous mixture consisting of solvent, particles, binder and additives, each of which has a different influence on the dope characteristics. The typical process to prepare a homogeneous mixture is following several steps in sequence: (1) mixing a dispersant with a selected solvent in a container; (2) adding ceramic particles which must be well dispersed by a sieve; (3) adding milling balls to homogenize the particle dope; (4) adding polymer binders and additive and (5) degassing the dope before the spinning process.

The major factors to form a homogeneous spinning dope are the particle sizes and their distributions, the choices of additives and solvent. Using a mixture of large-size and small size particles can increase the packing density and hence influence the

porosity, pore size, pore size distribution and mechanical strength of the final membrane.

Additives such as dispersant, defoaming agent and plasticizer are used to improve the stability of dispersion in spinning dope. The stability of dispersion depends on the ability of the dispersant to break the surface interaction (i.g. Van der Waals forces, electrostatic forces, steric interaction) between particles to allow them to retain separately. Zurcher et al have systematically studied the properties of YSZ dopes by testing more than 10 different dispersants. [38] They concluded that the dispersant of the Solsperse 3000 is the most suitable for YSZ dope. In addition, it should be noted that the selected additive can be burned away without leaving ash or tar during the sintering process. The amount of additive used should be as small as possible to allow more particles packing in spinning dope.

Solvents using the phase inversion technology must be able to dissolve additives and binders and must exhibit a higher exchange rate with nonsolvents (coagulant). The exchange rate between solvent and nonsolvent has an effect on cross sectional structure of membrane precursor and further affects the structure of the final ceramic membrane.

After mixing, the homogeneity and viscosity of the resulting dope also play important roles in the structure of membrane precursor. The homogenous dope is an essential requirement for forming of ceramic precursors as it can eliminate structural defects and stress centres. Kingsbury and Li found that viscosity is a critical factor in determining the structure of membrane precursor for ceramic dope system. [39] In general, the viscosity of spinning dope is higher than that of casting dope used to form equivalent flat sheet membrane as hollow-fibre membrane must be able to withstand the applied force during the spinning process without collapsing. The minimum requirement of viscosity for polymeric hollow-fibre membrane should be 10 poises to allow hollow-fibre membrane to be spun or drawn without collapse into droplets. [40]

2.3.2 Spinning process

Figure 2.6 shows the spinning apparatus and the structure of spinneret. [40] The prepared spinning dope is pressurized at a constant pressure through a tube-in orifice spinneret while internal coagulant is pumped through the centre of the spinneret, forming a hollow and longitudinal tube. The tube then travels to the coagulation bath and is turned up at the end. The forming of membrane precursor results from the exchange between solvent and non-solvent in the case where the solvent diffuses out of the spinning dope, while nonsolvent diffuses into the dope. There are many factors could affect the exchanging rate as shown in Figure 2.5. In a ceramic dope system, it could also involve the movement of different sized ceramic particles during the exchanging phenomenon, resulting in a more complex exchange and movement mechanism. Hence, the ratio between small and large size particles is considered to be an important factor in the preparation of ceramic hollow-fibre membrane. The detail of particle movement in the ceramic membrane fabrication has been studied elsewhere. [41] The spinning process is very similar to the extrusion process. The main difference is that the spinning dope is in liquid form and the resulting membrane exhibits an asymmetric structure because of the phase inversion of specimen in the solution.

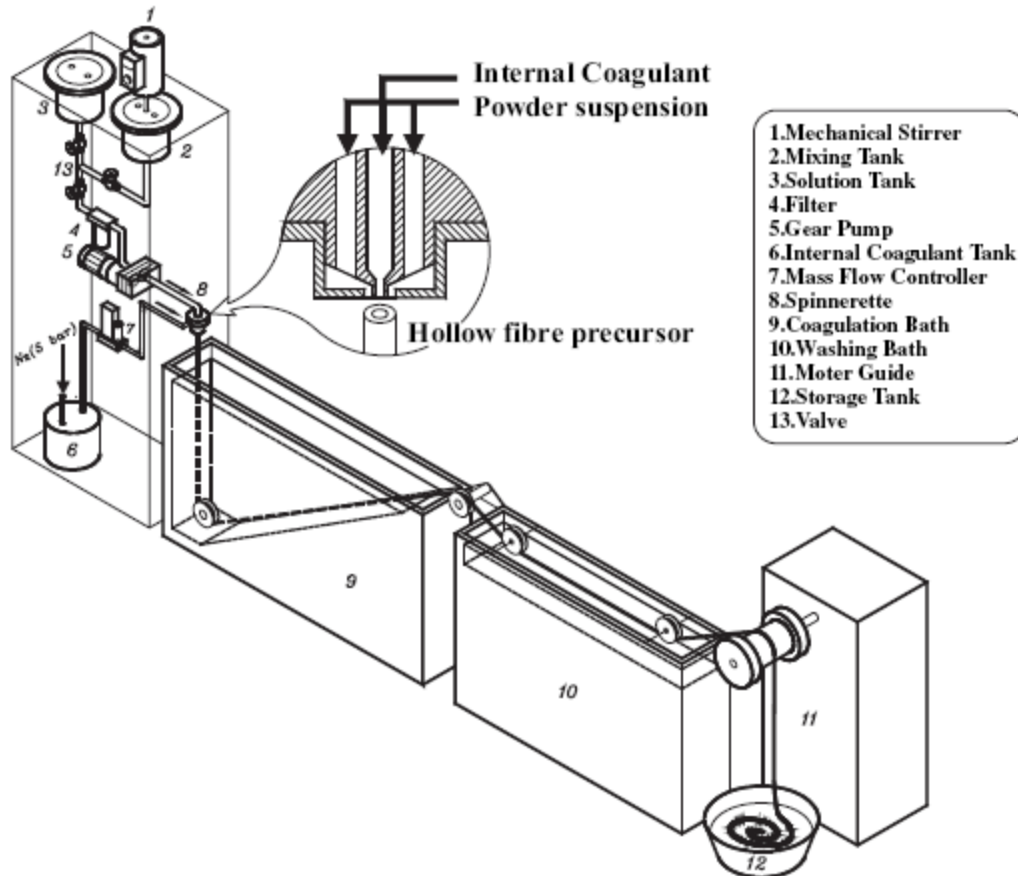


Figure 2.6 Schematic diagram of spinning process

2.3.3 Sintering process

After shaping, the membrane precursors, including ceramic particles, residual organic solvent, dispersant and binder often undergo a high temperature treatment, named sintering process or calcination. Ideally the sintering process serves to join powder particles together without melting them. Therefore, the temperature at which sintering is usually carried out is in the range between approximately 50 to 80 % of the melting temperature of ceramic particles. For YSZ, with an approximate melting point of 2700 °C, the sintering temperature is roughly between 1300 to 2160 °C. Apart from ceramic particles, all other materials are burned away at the sintering temperature. Ceramic particles are joining and bonding together in the sintering process. The formation of strong bonds could provide mechanical strength for ceramic membrane.

The sintering process usually involves three stages. [9]

(1) Initial sintering: The initial stage consists of ceramic particle rearrangements and neck growth at contact points between particles, as shown in Figure 2.7 (b). The neck

growth between particles is led by at least six different mechanisms, including surface diffusion, lattice diffusion from the surface, vapor transport, grain boundary diffusion, lattice diffusion from the grain boundary and plastic flow. [42] The initial stage lasts until the radius of the grown neck has reached to 40 to 50 % of the particle radius. Linear shrinkage decreases around 3 to 5 % in this stage.

(2) Intermediate sintering:

In this stage, grain boundaries start to develop which bond ceramic particles and form pore channels. The pore channels exhibit along the grain edges, as illustrated in Figure 2.7 (c). As the stage continues the pores and pore channels are connected. As pores become unstable and pinch off leaving the isolated pore, it is considered that the intermediate stage is over and final stage is starting. The intermediate stage, leading to a major shrinkage of ceramic membrane, is the main part in the sintering process.

(3) Final stage sintering:

In the beginning of the final stage, the pores continue shrinking, some of which pinch off and become isolated at the grain corners, as shown in Figure 2.7 (d). In the end of the stage, the pores gradually eliminate from membrane surface and the membrane almost loses all the porosity. Grain size mainly increases in this stage.

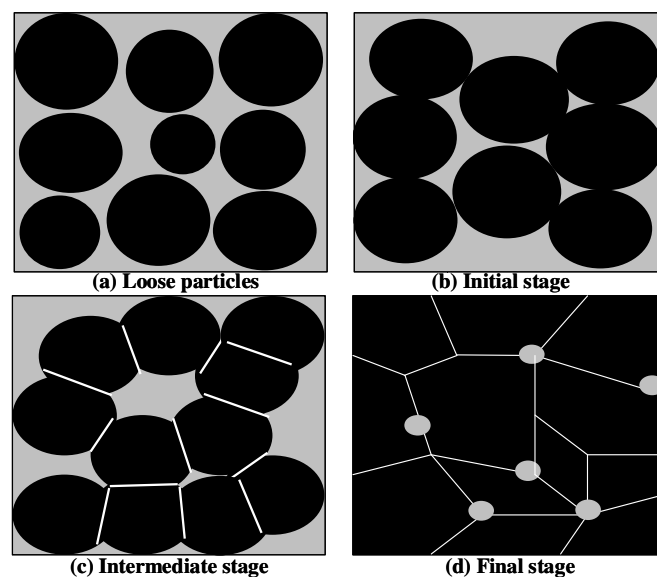


Figure 2.7 Development of ceramic microstructure during sintering process

The formations of microstructures (e.g. pores or pore channels) are mainly affected by the sintering process which theoretically can be controlled by a sintering profile. A typical sintering profile for industrial applications consists of six steps.

Step 1: removal of binder:

Most organic compounds such as solvent, binder and additive and some volatile materials such as absorbed water are burned away in the step 1. The heating rate should be carefully controlled as a rapid heating may cause boiling and evaporation of organic compounds. The heating rate is often below 2 °C per minute. The hold temperature in this stage is around 400 to 600 °C, since most organic binders can be decomposed in this temperature range.

Step 2: low temperature soak

This step is generally carried out in a heterogeneous powder system where may have dopant and/or varied ceramic particles. This step can promote chemical homogenization or the solid state reactions of ceramic materials in the system. The chemical homogenization may involve a small amount of dopant react into ceramic particles. In this step, the densification of powder does not occur and the microstructure is not modified yet.

Step 3: heating up to the sintering temperature

Ceramic powder is compacted and heated up to isothermal sintering temperature in this step. The heating rate should be carefully controlled to achieve a required microstructure in the final membrane. The heating rate is usually in the range of 1-10 °C as it is limited by the size and amount of specimens as well as the thermal characteristics of the furnace. In general, a faster heating rate can develop a denser outer surface. However, the faster densification can also cause cracks and defects of the membrane. In industrial applications, a slower heating rate (i.e. long heat-up period) is usually required to avoid these problems.

Step 4: Isothermal sintering

An ideal isothermal temperature should be chosen as low as possible and achieves the densification within a reasonable duration which is usually less than 24 hours. A higher sintering temperature can lead to faster densification and simultaneously the

rate of grain growth also increases. The increased grain size may lead to abnormal grain growth where pores are trapped inside large grains. An example of trapped pores in larger YSZ grain is shown in Figure 2.8. The example was performed at a sintering temperature of 1500 °C which is higher than a suggested sintering temperature of 1400 °C for densification of YSZ membrane. [41, 43]

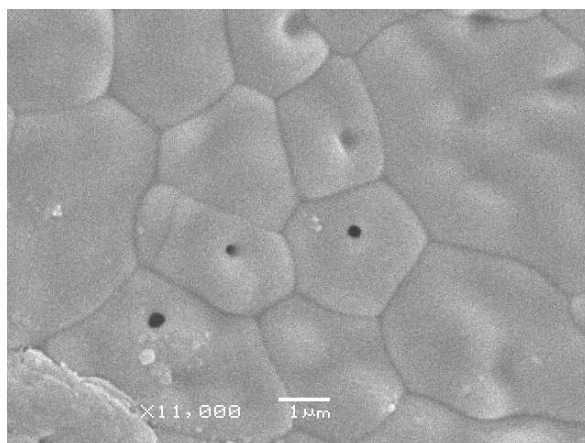


Figure 2.8 Trapped pores in larger grain on the inner surface of YSZ hollow-fibre membrane which was sintered at 1500 °C for 3 hours

Step 5 Cooling down to room temperature

A cooling step with a suitable cooling rate is carried out after densification. In this step, the ceramic membrane is cooled to room temperature or in some cases to an annealing step where thermal stresses can be relieved. The cooling rate cannot be too fast for most ceramic specimen in order to prevent the occurrence of cracking. In heterogeneous ceramic systems, the cooling rate is particularly important as it can influence the precipitation between different phases and the morphology of precipitates. The cooling rate in some ceramic devices (e.g. varistors and some ceramic capacitors) is considered to be an important parameter to achieve a desirable microstructure. [44]

Step 6 Annealing

Some materials require an isothermal heat treatment (annealing) at a temperature which is below sintering temperature to relieve thermal stresses, modify the chemical composition or microstructure before cooling down to room temperature. The step is commonly performed for the materials which contain a glassy matrix or involve a very large volume change such as the crystallographic transformation. The annealing

step is also an important step to modify the microstructure of ferrite, Si_3N_4 and Sr-doped TiO_2 to improve the high temperature tensile strength (creep resistance). [42] The difference of grain microstructure was also observed at different annealing temperatures and annealing duration for Sr-doped TiO_2 system. [44] It should be noted that the shape (e.g. disk, fibre or tube) and macrostructure (e.g. symmetric or asymmetric structure) of the membrane is still retained after the sintering process.

In addition to sintering profile, gaseous atmosphere and applied pressure are also considered important factors for the sintering process. Recently, a new sintering process named spark-plasma sintering (SPS) or pulse electric current sintering has been reported by Balakrishnan et al and Takeuchi et al. [45, 46] The SPS process can produce dense ceramic or metal in a very short time. The process is considerably similar to the traditional hot-pressing process. A uniaxial force (approximately 30-50 MPa) is applied on the powder loaded in a graphite die and an electric current of 800-1000A is simultaneously passed to heat the powder, instead of being heated by an external source. The SPS process can compact powder and uniformly heat the powder to achieve a high density membrane at lower a temperature (1100~1300 °C) within a few minutes (1~30 minutes). The mechanical strength of the YSZ membrane is considerably stable at 1000 °C for 1000 hours.

2.4 Mechanical strength

Mechanical strength is often examined by using the bending test due to its low cost and simple operation. As shown in Table 2.1, YSZ material exhibits a very high mechanical strength. However, the mechanical strength of YSZ membrane relies on many factors during the fabrication such as particle size, packing density, microstructure, porosity and grain size.

In general, high packing density and dense structure would offer higher mechanical strength, whereas low packing density and porous structure have lower mechanical strength. It has been found that the addition of nano-size ceramic particle can enhance the packing density and result in smaller pores and substantial flaw-free membranes. [31, 32] Carter et al also found that the mechanical strength of ceramic membrane relies on its porosity. [2] An external stress cannot be uniformly applied through

porous membrane as membrane pores act to concentrate stress. The mechanical strength is also affected by grain size. Large flaws in between large grains also act as stress concentrators and affect the mechanical strength.

Other factors such as fabrication routes, fabrication conditions, specimen size and the test method are also important to the mechanical strength of ceramic membrane. For example, large and strong agglomerates ($>100\text{ }\mu\text{m}$) in YSZ powder can cause flaws in the membrane preparation, resulting in a poor mechanical strength of the membrane.

In this study, a three bending test is used to study the mechanical strength (i.e. flexure strength) of ceramic membrane. This testing method is commonly used as a criterion for the applications of ceramic hollow-fibre membranes. [31, 32]

2.5 Ionic conductivity

The oxygen ionic conductivity of YSZ was first found by Nernst in 1899. [47-51] An ideal fluorite structure of partial-stabilized zirconia is shown in Figure 2.9. [52] The oxygen ionic conductivity results when an oxygen ion hops from an occupied to a vacant lattice or an interstitial site.

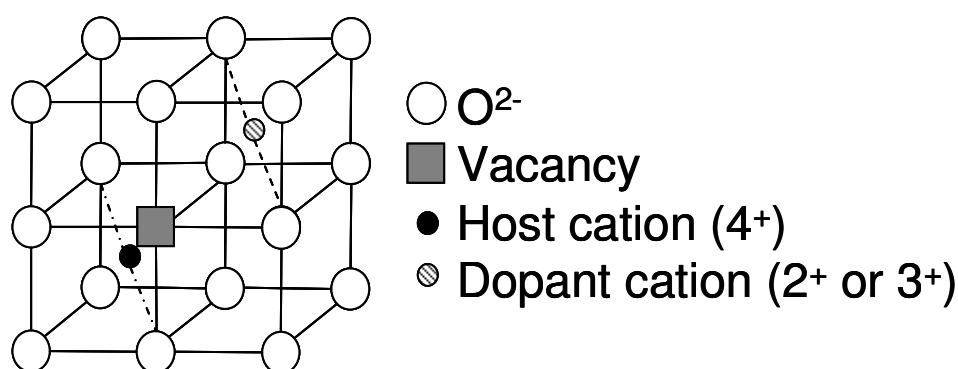


Figure 2.9 Ideal fluorite structure of partial-stabilized zirconia

The oxygen-ion vacancy structure has been proven by different technologies such as X-ray, neutron diffraction, and diffusivity of oxygen ions in stabilised zirconia. [48-51] A high oxygen-vacancy concentration in stabilised zirconia enhances a high oxygen ion mobility, leading to a high ionic conductivity. At high temperature, the ionic conductivity of YSZ with the fluorite structure is higher than sulphuric acid at $18\text{ }^{\circ}\text{C}$.

[47] The oxygen ionic conductivity of YSZ is influenced by several factors: (a) dopant concentration: The maximum conductivity of YSZ material can be achieved by doping 8-10 mol % Y_2O_3 into zirconium oxide. [52, 53] However, further increasing the amount of Y_2O_3 in zirconia can result in a lower ionic conductivity due to the steric blocking of larger cations. [54, 55]; (b) temperature: The relationship between conductivity and temperature for YSZ follows Arrhenius equation below: [56]

$$\sigma = A \exp(-\Delta H/RT) \quad (2.1)$$

where σ is the conductivity, T is the temperature, A is approximately independent of temperature ($\text{ohm}^{-1}\text{cm}^{-1}$) and ΔH is the activation enthalpy (kcal mol^{-1}). According to the equation, the conductivity of YSZ is reciprocal to temperature. A high operating temperature can result in a high conductivity. The ionic conductivity of YSZ exhibits over a wide range of temperature in between 550 °C to 2100 °C. [57, 58] However, the operating cost in industrial applications could be increased at high operating temperatures. A recommended operating temperature for YSZ electrolyte is between 600 °C to 1000 °C. [17]; (c) atmosphere: the oxygen ionic conductivity of YSZ is independent of oxygen partial pressure in the range from 10^{-22} to 1 atm. [17] In this range, the ionic transport number is very close to unity and the electronic conductivity can be negligible. However, as the oxygen partial pressure is lower than 10^{-30} atm, the electronic conductivity would increase and further influence the performance of YSZ electrolyte. [59] The present electronic current flowing through the YSZ electrolyte can cause the voltage losses in practical application. Therefore, the normal operating range of oxygen partial pressure for SOFC application is about 0.21 to 10^{-20} atm. [17]; (d) grain boundary: the ionic conductivity of YSZ consists of the grain (bulk) conductivity and the grain boundary-conductivity. [60] The grain-boundary conductivity is mainly affected by impurities and grain size. As the grain size is smaller than 5 μm , the grain-boundary conductivity is independent of the grain size and is much lower than grain conductivity by 100 times. [61] As the grain size is larger than 5 μm , the grain-boundary conductivity decreases with the increase of grain size. The grain-boundary conductivity also decreases with the increase of impurities concentration from about 0.1 wt% to 0.5 wt%. [62-65] The influence of grain-boundary is only considered at low or intermediate temperature (<500 °C). It has a

lesser influence on the conductivity in high purity of YSZ electrolyte at high operating temperature; (e) aging: some studies found that the conductivity of YSZ degrades within less than 1000 hours at approximately 1000 °C. [63-65] Hattori et al. have found that the influence of aging is mainly attributed to the gradual formation of fine tetragonal phase in cubic matrix. [63] A higher Y_2O_3 doping level ($> 9\text{mol. \%}$ YSZ) can eliminate the annealing aging and achieve a steady conductivity. In practical SOFC applications where YSZ electrolyte is usually prepared from 10mol. %YSZ, the conductivity aging effect can be negligible. The degradation of a larger tubular SOFC designed by Siemens Westinghouse is less than 0.1% per 1000 hours. [66-69]

2.6 Applications

2.6.1 Solid oxide fuel cell

The most common application of YSZ is used as an electrolyte in SOFC. This is because of its high ionic conductivity and almost total absence of electronic conductivity. The ionic conductivity is stable against the wide range of oxygen partial pressure (from 10^{-30} atm to 1 atm). In addition, the mechanical stability at high temperature and relatively low cost are also the benefit of YSZ material.

A solid oxide fuel cell (SOFC) is an electrochemical cell that generates electricity directly from a gaseous fuel by electrochemical combination of the fuel with an oxidant across an ionic conducting oxide electrolyte. In a conventional thermal power system, the chemical energy of the fuel is transformed first to thermal energy, then to mechanical energy, and finally to electrical energy. For a SOFC, because of the electrochemical reaction, more of the chemical energy is converted into useful work. Such a device bypasses the conversion of chemical energy of fuel into thermal and mechanical energy, and thus achieves theoretical efficiency (100 %) significantly higher than that of conventional methods of power generation ($< 27\%$).

Figure 2.10 shows a SOFC scheme, containing anode, cathode, electrolyte and interconnecting wires. The characteristic of the electrolyte is an important factor to

SOFC design since the electrolyte must be chemically and thermally compatible with other components from room temperature to high temperature (600 to 1000 °C), while the ionic conductivity is still retained and is stable in both the reducing and oxidizing environments. In addition, the solid electrolyte should not exhibit corrosion and decay problems to eliminate SOFC management.

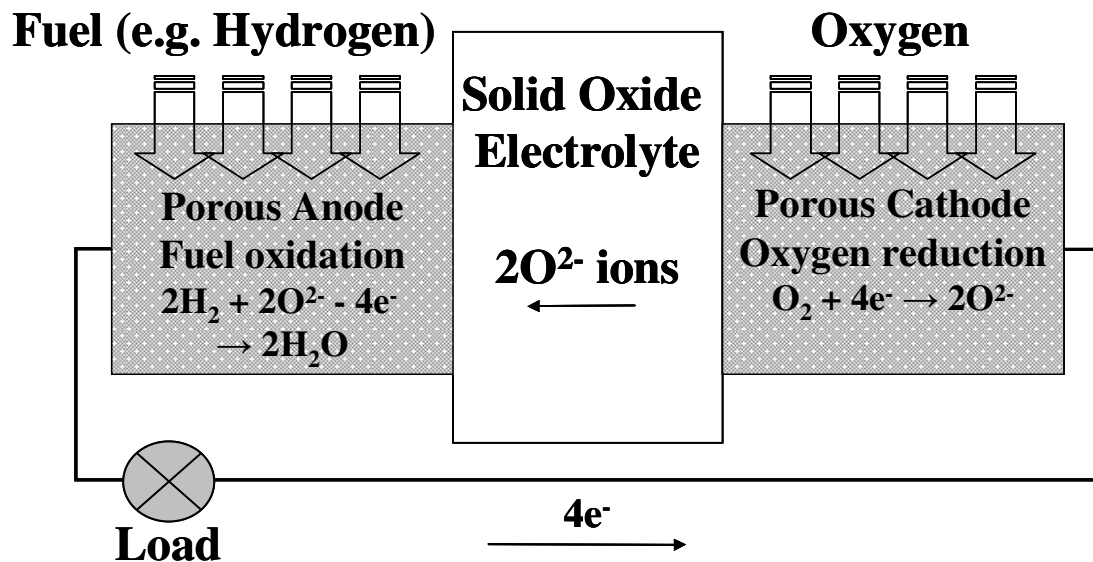


Figure 2.10 Scheme of solid oxide fuel cell

The configurations in SOFCs can be classified into two types: (1) external-supporting and (2) self-supporting. Both of them are required to be dense to prevent gas cross leakage and as thin as practicable to minimize cell resistance.

The external-supporting SOFCs offer thinner cell components, but interconnected materials and high-temperature seals must be stable during thermal cycling. Compared with the external-supporting SOFCs, the self-supporting design can offer better thermal cycling capability and cheaper assembling costs.

So far, one of the common self-supported SOFC is using an electrolyte as a support material. The typical thickness range of the electrolyte-supported SOFC made with YSZ flat sheet is thicker than 700 μm whereas for the tubular configuration, the thickness is reported in an approximate range between 200 and 600 μm . [66, 67, 69] The present studies of electrolyte-supported SOFC can provide reliable power densities while the operating temperature must be above 700 °C. To reduce the

operating temperature, some studies have focused on finding other ionic conducting materials. The ionic conductivities of other materials at different temperature are shown in Figure 2.11. [66, 70]

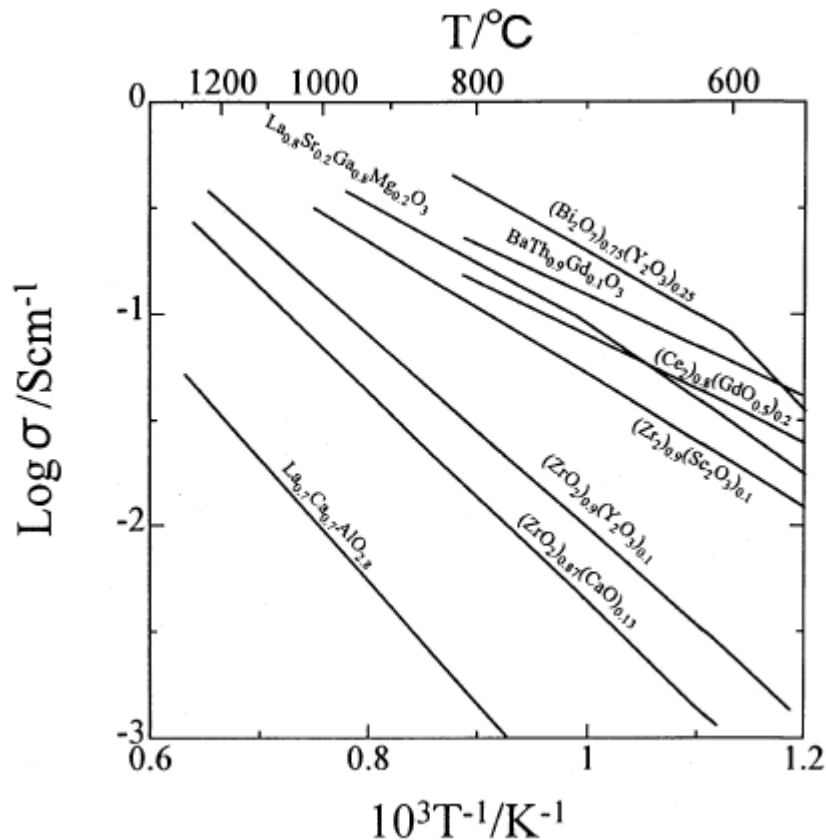


Figure 2.11 Ionic conductivities of different materials at varied temperature [66, 70]

As based on the same ionic conductivity, different materials such as $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) or $\text{Bi}_2\text{O}_3\text{-MO}$ (where M is calcium, strontium, or barium) show lower operating temperature than YSZ material. However, these materials are more expensive than YSZ and they are not as strong as YSZ to be an electrolyte-support for a SOFC. Alternatively, some studies were focusing on the geometries and constructions of SOFC to increase the power density per unit and hence to allow economic mass production cost. Two common geometries for the SOFC are planer and tubular. The details of these two geometries are described below.

Planer geometry

Planer geometry has received much attention since the design can provide simple cell construction and multiple fabrication options. For examples, the planer cell components can be fitted into square, rectangular, circular or hexagonal. The electrolyte layer is often the thickest component of planer SOFC. A typical YSZ electrolyte-support SOFC in planer geometry is above 700 μm . [69, 71] Another advantage is that planer stack design can provide higher power density ($\sim 2\text{MW.m}^{-3}$) than tubular design ($\sim 0.3\text{MW.m}^{-3}$) [52, 72] since the cell components can be made very thin to minimize internal ohmic loss of the planer SOFC. Other characteristics such as that it is easier to incorporate with interconnects and lower fabrication cost also serve as advantages of planer SOFC.

However, the planer SOFC requires high temperature seals to prevent the gas leakage at the edges of stack or inside the gas ports of the plates during operating. The high temperature causes the inevitable thermal expansion mismatches between the sealants and stack ceramics. Further, the sealing problem may limit the dimension of SOFC stack. The development of robust sealing materials is still crucial to long term performance and reliability of the planer stack. [73]

Tubular geometry

Early tubular SOFC was fabricated on a CaO-stabilized ZrO_2 support. [74] The CaO-stabilized ZrO_2 tube was only used as a structural membrane to provide mechanical integrity for tubular SOFC. Cathode, electrolyte and anode were sequentially coated on the support tube. Cathode was casted by simple dip-coating method. The electrolyte layer (YSZ) and anode (Ni) were deposited by using relatively expensive methods such as electrochemical vapor deposition (EVD) and plasma spraying. However, the thick support tube with 20 mm thickness limits the amount of oxygen which can react at the cathode / electrolyte interface and further influence the SOFC performance.

An improved tubular SOFC was fabricated from a cathode support tube by Siemens Westinghouse. The electrolyte layer (YSZ) and anode (Ni) were still deposited using the EDV method. [75] The outer diameter of the cathode-support SOFC is about 22

mm. The cathode-support SOFC stack has been operated for about 5,000 h at 1,000 °C and has shown stable and excellent performance. [74]

The evident advantage of tubular SOFC is that this design can avoid the requirement of high temperature seals. Figure 2.12 illustrates single laboratory-scale tubular SOFC system. The sealing part which is used to separate oxidant (air) and fuel can be established in the room temperature (i.e. outside the high temperature area), so the problem with gastight seals for ceramic at high temperatures can be eliminated. In addition, from a mechanical engineer perspective, the tubular design provides the freedom to expand and contract without constraint.

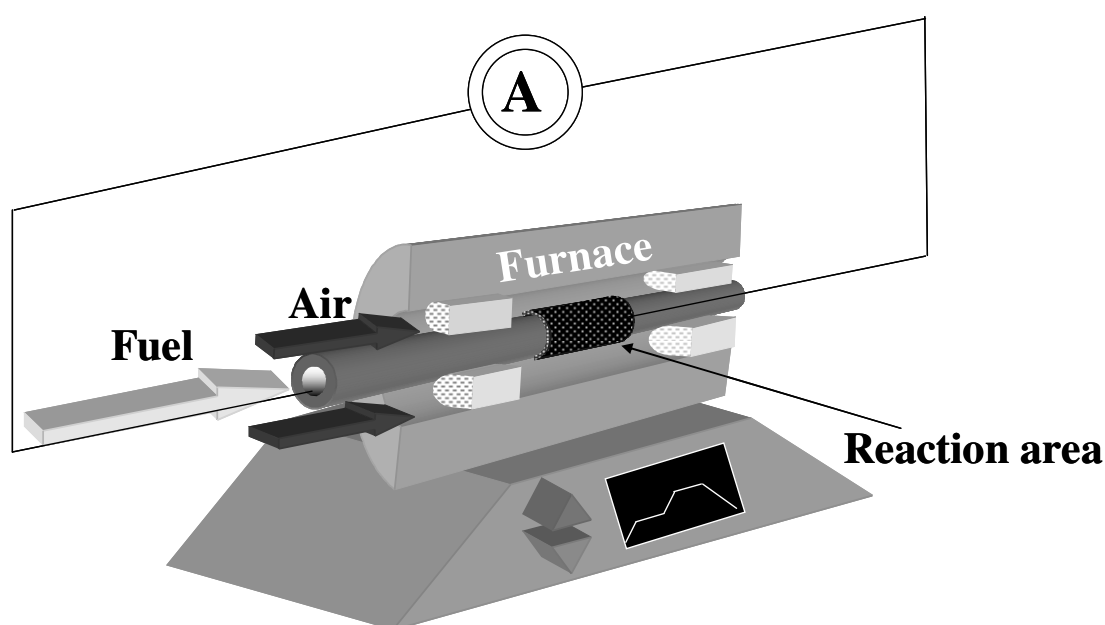


Figure 2.12 Scheme of tubular solid oxide fuel cell

However, the limitation of tubular SOFC is that the powder density cannot be effectively increased as the tubular design adds weight and volume to SOFC. In addition, the EVD process used in the fabrication of tubular SOFC severely restricts the selection of dopants for the electrolyte.

Recently, studies have focused on the size reduction for the tubular SOFC. Coe et al. have developed small diameter tubular SOFC to overcome the lower power density problem. [76] The outer and inner diameters of the electrolyte-support SOFC are 2.15 and 1.65 mm, respectively. The anode and cathode were simply dip-coated using

nickel metal paste and lanthanum strontium manganite (LSM) ink, respectively. The power density of the smaller tubular SOFC is approximately ten times higher than the cathode-support SOFC developed by Siemens Westinghouse as shown in Table 2.2. [77] The power density of small diameter tubular can compete with which of the planer stack.

Table 2.2 Effect of varied SOFC dimension on power density

Outer diameter of tubular SOFC (mm)	Surface area of the stack (m ² m ⁻³)	Estimated power density (MW m ⁻³)
22	100	0.3
2	820	2
1	1,640	4

However, as can be seen in Figure 2.13, the adhesion between anode and electrolyte-support in the tubular SOFC is not stable. [76] The poor adhesion can cause the failure of electrochemical performance. In addition, the thickness of the electrolyte in the small tubular SOFC is approximately 250 μm which is considered to be too thick for SOFC. [78, 79] Although the thick electrolyte-support can provide substantial mechanical strength for practical applications, the electrolyte could increase internal resistance and further influence the electrochemical performance.

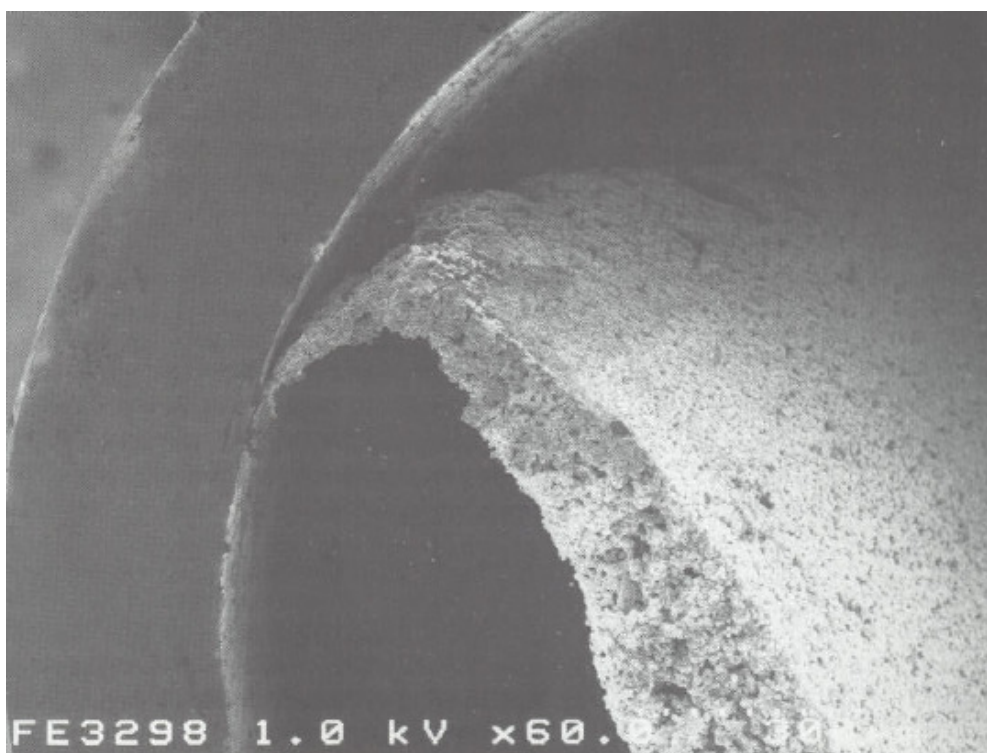


Figure 2.13 SEM image of the interface between electrolyte and anode [76]

Recently, an anode-support microtubular SOFC with 1.6 mm diameter has been developed and performed at intermediate temperature region under 600 °C. [80] The microtubular SOFC consists of typical components, an anode made of NiO-Gd doped ceria (GDC), an electrolyte made of GDC and a cathode made of (LaSr)(FeCo)O₃ (LSCF)-GDC. In order to provide substantial strength, the porosity of the anode support is relatively lower than other anodes of self-support SOFCs. The low porosity of anode-support SOFC limits the amount of fuel which can react at the anode / electrolyte interface and further influence the SOFC performance. [81] In addition, a reduction of Ce⁴⁺ to Ce³⁺ occurs as NiO reduces to Ni by hydrogen at above 450 °C, thus causing mixed oxide-ion and electronic conduction in the electrolyte. This leads to an energy loss and results in a low open-circuit voltage (OCV) which is a disadvantage for practical applications. [82]

Effective methods to avoid the reduction of cerium have been developed by Daisuke et al and Inoue et al. [82, 83] Inoue et al have found that the OCV was increased as an YSZ thin film was sputtered on the fuel side of the GDC electrolyte. Similar observations have been also found by other research groups. [84, 85] This is because the YSZ sputtering film can effectively suppress the reduction of cerium by fuel gas.

Other materials such as $\text{BaCe}_{1-x}\text{M}_x\text{O}_{3-\alpha}$ (M is the dopant cation in electrolyte used) can be also used as a coated layer to improve the decrease of OCV. [82] It should be noted that an additional thermal treatment (sintering) for the coated layer (either YSZ or $\text{BaCe}_{1-x}\text{M}_x\text{O}_{3-\alpha}$) can be required for the anode-support SOFC.

2.6.2 Membrane contactors

Traditional gas/liquid and liquid/liquid contacting operations are carried out by using tower, packed column or mixer settler. [86] The major challenge in these devices is to maximize the mass transfer rate by providing as much contacting area as possible. For packed columns, different packing materials, the shapes of the packing materials and packing configurations have been widely studied in order to increase the contacting area in industrial applications. Although the packed columns have been performed in chemical industries for many decades, there are still some problems which cannot be solved due to the design and operation of the packed column. For example, a flooding problem can take place at high liquid flow rate and an unloading problem at low liquid flow rate. These problems lead to more energy-consuming and other difficulties in the operation.

In membrane contactor, the contact of two fluid phases occurs at membrane pores. Two fluids flow on the opposite sides of the membrane and thus can be operated independently. Mass transfer between two fluid phases takes place at the contacting area (i.e. membrane pores). The driving force of the mass transfer is a concentration gradient rather than a pressure gradient, though a very small pressure drop may require retaining the contact of two fluids at the membrane pores.

The use of membrane in membrane contactor is unlike other membrane processes which highly rely on the selectivity of membrane. Instead, a non-selective membrane with larger pore size is preferred to be use in membrane contactor as this membrane can offer lower mass transfer resistance. [87, 88]

In practical application, most membrane contactors are packed with hollow-fibre membranes because of their much larger interface area per unit volume than other

membrane configurations such as flat-sheet or tubular membranes. The details of hollow-fibre membrane contactors (HFMC) are discussed in the following section.

Advantages and disadvantages of membrane contactors

The advantages of membrane contactors are summarized below:

(1) Easy operation: The flows of two fluids on the lumen and shell sides of hollow-fibre membrane can be manipulated independently. This independent manipulation can avoid some problems such as foaming, flooding, unloading, entrainment etc., which are commonly found in traditional devices. Also, emulsion formation can be avoided as gas does not directly disperse into liquid phase.

(2) Economical efficiency: The larger surface area/volume ratio of a hollow-fibre membrane module (range from 3000 to 8000 m² m³) is more economical than a packed column (about 800 m² m³). [89] According to studies by Falk-Pedersen et al., membrane contactors are smaller and lighter than packed columns by 72% and 66%, respectively. [90] Feron and Jansen also demonstrated a membrane contactor could lead to a near ten-fold reduction in a conventional absorber size for the removal of CO₂ from fuel gas. [91]

(3) Easy scale-up: membrane modules are usually operated linearly and therefore scale-up can be achieved simply by adding /connecting membrane modules. With the modular design, the construction of membrane contactors can be applied over a wide range of capacity from very small to very large.

(4) Easy prediction: The interfacial area of membrane contactor is fixed and constant and does not change with different operating conditions such as fluid flow rates and operating temperature. This makes it easier to predict or simulate the performance of membrane contactors.

(5) Easy maintenance: There are no moving parts in membrane contactors. This is beneficial for regular maintenance.

(6) Low liquid/solvent hold-up: The hold-up liquid/solvent is relatively lower than conventional packed column as liquid/solvent is efficiently used and uniformly

distributed throughout the membrane contactor. This feature is very important for systems that use expensive or hazardous liquids/solvents.

(7) Suitable for viscous fluid: Membrane contactor has been found where the performance is better than traditional bubble column when a viscous liquid is used as an absorbent. This is because the interfacial area of the membrane is not influenced by increased viscosity. In contrast, the interfacial area of bubble column is reduced with the increase of liquid viscosity and further influences the performance of the bubble column.

On the other hand, membrane contactor also shows some drawbacks which are listed below:

(1) Interior mass transfer coefficients: In membrane contactors, an additional resistance which is not present in conventional devices is the resistance of the membrane itself (e.g. large thickness and low permeability). However, the resistance is not always important. The studies of membrane technologies and fabrications have been improved dramatically. Membrane contactors packed with thin and high permeable membranes have been developed. [92, 93] In addition, the resistance can be also diminished by the larger interfacial area of hollow-fibre membranes. [87] Therefore, the membrane contactors can still show better performance than conventional devices.

(2) Bypassing: Shell-side membrane contactors could reduce the efficiency of contactors, especially in large scale applications. However, the efficiency can be improved by optimizing the module design and using baffled modules.

(3) Sealing: Sealing material is very important in the fabrication of HFMC. A good sealing material can prevent leaking from the joining part between hollow-fibres and module as well as protect the hollow-fibre membranes. Materials such as polyurethane, polyolefin, silicon rubber etc. are often used in sealing agents for HFMC. [94, 95] The selection of sealing material is more critical as it could directly contact with organic solvents in some applications.

(4) Fouling: As other membrane processes, membrane contactors also have a fouling problem. Nevertheless, the problem in membrane contactor is considered small because the main driving force in membrane is concentration gradient rather than pressure gradient. Therefore, the accumulation of solute in membrane contactors is much less than other membrane processes.

(5) Membrane durability: Most membrane contactors are packed with polymeric membranes which have limited uses in chemically harsh environments or at elevated temperature. Some studies have also found that the polymeric membranes were swelled after contact with organic solvents. [96, 97] Moreover, most membrane contactors were limited to use at low or ambient temperature.

As discussed above, membrane contactors show numerous advantages over traditional devices such as packed column or bubble column. Although there are still some disadvantages, almost most of them can be improved by careful selections of membrane materials and module designs. Therefore, many researchers and studies have focused on the applications of membrane contactors. One of the successful applications is applied to absorption process. The principle of membrane absorption is discussed below.

Principle of membrane absorption

In a HFMC, the gas and liquid phases flow on the different sides of the hollow-fibre membrane, as shown in Figure 2.14. The flowing gas phase is absorbed by moving liquid phase at the membrane pores (i.e. at the contacting area). The absorption process includes physical absorption, chemical absorption or a combination of both absorptions.

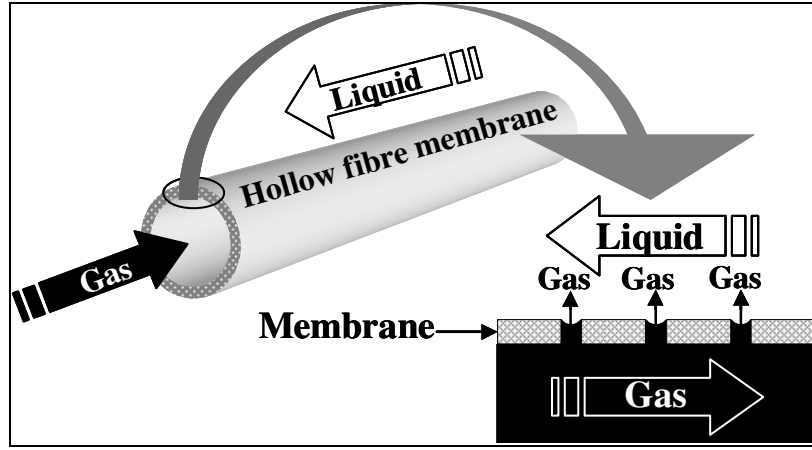


Figure 2.14 Scheme of a hollow-fibre membrane contactor

The mass transfer process on the contacting area follows three steps: (1) gas diffuses from bulk gas phase to the surface of membrane; (2) gas diffuses through membrane pores into liquid phase; (3) liquid phase absorbs gas. The overall mass transfer coefficient can be estimated by following equation (2.2) [98]

$$K_G = \frac{Q_g}{A} \ln \left(\frac{C_{\text{CO}_2, \text{in}}}{C_{\text{CO}_2, \text{out}}} \right) \quad (2.2)$$

where K_G is the overall mass transfer coefficient for CO_2 (m s^{-1}); A is the gas-liquid interfacial area; Q_g is the gas flow rate ($\text{m}^3 \text{s}^{-1}$); $C_{\text{CO}_2, \text{in}}$ and $C_{\text{CO}_2, \text{out}}$ are the CO_2 concentrations in the gas phase at the inlet and outlet, respectively.

Membrane absorptions are widely used in the treatment of contaminated gas or flue gas. Among them, many studies have focused on CO_2 absorption into amine solution as CO_2 has been considered as one of the main greenhouse gases. The dimension of a membrane contactor is much smaller than a traditional packed column, leading to higher efficiency per volume. The process has a large scale-up pilot plant in the Netherlands, and Canada. [91, 99-102] They have successfully demonstrated that the pilot plant made by membrane contactor can efficiently remove CO_2 from fuel gas. With the same performance of CO_2 removal, the size of a traditional packed column is 10 times larger than a commercial membrane contactor. [91]

The liquid flow rate in membrane absorption can be higher by an order of magnitude than traditional packed columns as the gas and liquid flow independently in membrane contactors. The higher liquid flow can allow maximum utilization of absorbent capability, resulting in a higher overall mass transfer which was observed 9 times higher than traditional paced column. [100]

There are some other gaseous impurities such as H₂S and SO₂ which also need to be removed from contaminant stream or fuel gas to comply with environmental regulations. Studies have proven that the laboratory-scale PVDF hollow-fibre membrane contactors can be used to effectively remove H₂S or SO₂ from flue gas into aqueous Na₂CO₃ or NaOH. [92, 98, 103, 104] The removal efficiency of H₂S in PVDF hollow-fibre membrane contactor was nearly 100%. [98]

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Chapter 3 Ceramic asymmetric hollow-fibre membranes—One step fabrication process

Abstract

Ceramic hollow-fibre membranes which have an asymmetric structure have been prepared in one step, using an immersion induced phase inversion technique. With this method, membranes with a high surface area per unit volume ratio can be produced, while production cost is dramatically reduced. Yttria-stabilised zirconia (YSZ) is selected as a membrane material, as it is relatively inexpensive and has superior mechanical strength as well as oxygen ion conducting properties. Therefore, both the porous and non-porous membranes prepared from the YSZ have potential applications. For example, the porous YSZ membranes can be used for fluid separations in harsh environments where normal polymeric membranes cannot be sustained, while the non-porous YSZ membranes can be applied as a solid electrolyte in electrochemical devices such as solid oxide fuel cells, oxygen pumps and chemical gas sensors. Gas permeation analysis suggests that non-porous YSZ hollow-fibre membranes can be prepared at sintering temperature of 1400 °C or greater, below which the membrane contains pores. Pore sizes of the YSZ porous membrane prepared fall into the pore size range of ultrafiltration membranes. However, the surface porosities of the membranes prepared from two-population sized particles at sintering temperatures of 1200 °C and 1400 °C are around 5000 m⁻¹ and 300 m⁻¹, respectively. The former is comparable to polymeric membranes, while the latter is an order of the magnitude smaller.

3.1 Introduction

In general, a ceramic membrane can be described as a permselective barrier or a fine sieve. The permeability and separation factor of a ceramic membrane are the two most important performance indicators. For porous ceramic membranes, they are typically governed by thickness, pore size and surface porosity, while for dense ceramic membranes, the principle for permeation and separation is more complex, depending on properties of the membrane materials and the membrane surfaces. Ceramic membranes are usually asymmetric or composite type consisting of several layers of

one or more different ceramic materials. They generally have a macroporous support, one or two mesoporous intermediate layers and a microporous (or a dense) top layer. The bottom layer provides mechanical support, while the middle layers bridge the pore size differences between the support layer and the top layer where the actual separation takes place. Commonly used materials for ceramic membranes are Al_2O_3 , TiO_2 , ZrO_2 , SiO_2 , etc. or combination of these materials. Most of the commercial ceramic membranes are in disc, plate or tubular configuration. They are usually assembled in a plate and frame module using disc or sheet membranes or in a tubular module using membrane tubes. In order to increase the surface area-to-volume ratio, giving more separation area per unit volume of membrane element, alumina multi-channel monolithic elements have been developed. [1] These monolithic elements can be combined into modules. Hsieh [2] reported that the surface area-to-volume ratios are around $30\text{--}250\text{ m}^2\text{ m}^{-3}$ for tubes, $130\text{--}400\text{ m}^2\text{ m}^{-3}$ for multi-channel monolithics and up to $800\text{ m}^2\text{ m}^{-3}$ for honeycomb multi-channel monolithics. Currently, ceramic membranes can only be achieved through multiple steps. A support layer is first prepared to provide the membranes with mechanical strength, followed by coating one or more intermediate layers on the support layer, before a final separation layer can be fabricated. Each step involves a high temperature heat treatment, making the ceramic membrane fabrication extremely expensive. Clearly, combining the multiple steps into a single step is desirable in cutting production time and costs, and hence membrane price. In addition, the membrane or membrane system price could be further reduced if the membrane can be prepared in hollow fibre geometry, as it provides the largest membrane area per unit volume ratio. [3]

Currently, most ceramic asymmetric/composite membranes have been prepared through a multiple step process described above. Literature information in discussing the preparation of asymmetric/composite ceramic hollow-fibre membranes is very scarce. de Jong et al. [4] attempted to use a triple orifice spinneret to spin two particle suspensions containing different sized Al_2O_3 particles at the same time, aiming to achieve a single step production of asymmetric ceramic hollow-fibre membranes. Li et al. [5] believed that a single step production of asymmetric ceramic hollow-fibre membranes can be simplified using a conventional tube-in-orifice spinneret as long as particles dispersed in the suspension show distributed particle sizes. They successfully demonstrated the production of a dense (non-porous) ceramic hollow-fibre membrane using an immersion induced phase inversion technique equipped with only a

conventional tube-in-orifice spinneret. [5] In this study, the fabrication of asymmetric ceramic hollow-fibre membranes in one step using an immersion induced phase inversion technique has been further elaborated. The membranes prepared using this technique show either non-porous (dense) or porous (ultrafiltration type) characteristics depending on the compositions of starting suspensions, fibre spinning parameters and final sintering conditions employed. Yttria-stabilised zirconia (YSZ) has been selected as the membrane material, as it is relatively inexpensive and has superior mechanical strength as well as oxygen ion conducting properties. Therefore, the membranes prepared from YSZ are robust with either a porous or non-porous structure. The porous membranes can be used in fluid separations in harshest of environments whereas normal polymeric membranes are unsustainable. The non-porous membranes can be used as a solid electrolyte in electrochemical devices, for example, in solid oxide fuel cells, oxygen pumps and chemical gas sensors. [6–8]

3.1.1 Basis in forming the ceramic asymmetric membrane in one step

The immersion induced phase inversion technique has been applied in production of polymeric membranes for many years and was first introduced by Loeb and Sourirajan. [9] The membranes produced by them [9] show an asymmetric structure: a dense and thin skin layer (about 25 μ m) integrated on a porous support of the same material. The dense skin layer shows a permselective property for separation of salt from seawater and is also thin enough for a high water flux. The porous substrate provides the mechanical stability for the membrane. Since then, this method has been one of the most common methods in the fabrication of polymeric membranes. Conceptually, membrane formation by phase inversion can be described in terms of a three-component system: nonsolvent, solvent and polymer. After immersing a polymeric solution into a nonsolvent bath, the solvent diffuses out of the polymer solution, while nonsolvent diffuses into the solution. This exchange of solvent and nonsolvent, in general, leads to a change in the polymer solution from a thermodynamically stable state to a metastable or unstable state. Then, liquid–liquid demixing takes place in the solution. When a polymer solution is in contact with a nonsolvent, the solvent in the polymer solution will diffuse out, resulting in the increase of the polymer concentration at the surface. The highly concentrated polymer layer at the surface reduces the exchange speed of the solvent and nonsolvent. Hence,

the polymer concentration in the sub-layer is lower than the polymer concentration in the surface layer. The further replacement of solvent by nonsolvent results in solidification of the polymer rich phase, and the asymmetric structure of the membrane is thus obtained. For a suspension system containing ceramic particles and polymer binders, the situation may be different. Figure 3.1 illustrates the movements of the ceramic particles during the phase immersion process.

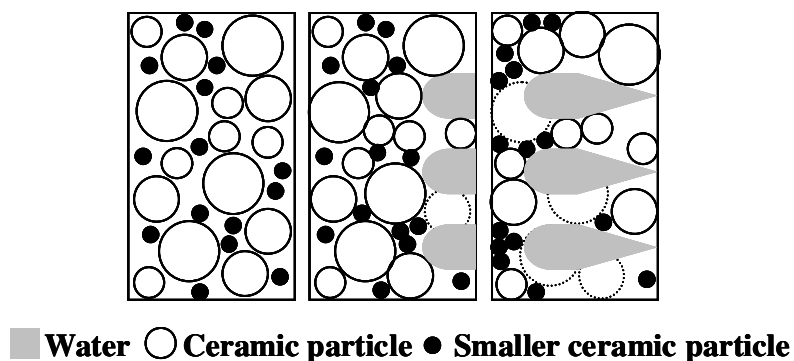


Figure 3.1 Sketch of ceramic particle movements

When a high viscous suspension is in contact with a low viscous hydrophilic nonsolvent (normally water), hydrodynamically unstable viscous fingering takes place, resulting in finger-like structures of the membrane substrate. Due to the high rate of water (invading phase) penetrating into the suspension containing hydrophilic particles of different sizes, it is logical to postulate that the smaller particles move along with water (invading phase) faster than the larger particles towards the surface and the ceramic membranes with a graded structure can be formed via the phase inversion technique as long as the particles with different sizes are used. A similar phenomenon has been observed by Chung et al. when preparing mixed-matrix membranes. [10] It follows that a good control of the ratio of small and large particles in the suspension and the exchange rate of the solvent and nonsolvent may tailor the membrane structure, which can only be prepared by multiple steps if conventional techniques are used.

3.2 Experimental

3.2.1 Materials

Commercially available 8 mol% yttria-stabilised zirconia powders with particle diameters (d_{50}) of 0.1 μm and 0.02 μm purchased from NexTech Materials Ltd., OH were used as membrane materials. Polyethersulfone (PESf) (Radel A300, Ameco Performance, USA) and 1-methyl-2-pyrrolidinone (NMP) (HPLC grade, Sigma–Aldrich) were used as the polymer binder and solvent, respectively. Polyvinyl pyrrolidone (PVP) (Acros Organics) and/or Solsperse 3000 (Noveon Inc., Ohio) were used as the additives. Tap water was used as external coagulant and deionised water was used as internal coagulant.

3.2.2. Preparation of YSZ hollow-fibre precursors

The immersion induced phase inversion/sintering technique was employed in preparing the YSZ hollow-fibre membranes. The detailed procedures were described in chapter 2 and elsewhere. [11] A spinneret with orifice-diameter/inner-diameter of 3.0mm/1.2mm was used to obtain the hollow-fibre precursors. The compositions of the suspensions for preparation of the YSZ hollow-fibre precursors are given in Table 3.1.

Table 3.1 Composition of YSZ starting suspensions for spinning precursors

	Composition (wt %)				
	YSZ (0.1 μm)	YSZ (20nm)	NMP	PESf	Additive
S1	55	--	38.5	6.0	0.5
S2	45	10	38.5	6.0	0.5
S3	45	--	47.1	7.3	0.6

The final YSZ hollow-fibre membranes were produced by heat treatment of the precursors in a CARBOLITE furnace with air. The furnace temperature was first increased at a rate of 2 $^{\circ}\text{C min}^{-1}$ to 600 $^{\circ}\text{C}$ where the thermolysis (i.e. removal of the polymer binder) was carried out for 3 h. The temperature was then further increased

to 1200–1500 °C at 5 °C min⁻¹ and was held for duration of 4 or 8 h for the final sintering. Finally, cooling was carried out to room temperature at a rate of 5 °C min⁻¹.

3.2.3. Characterisation of YSZ hollow-fibre membranes

Scanning Electron Microscopy (SEM, JEOL JSM-5610LV, Japan) was employed to study the morphologies of the YSZ membranes. The hollow-fibre precursor was cooled in liquid nitrogen for approximately 5 min, enabling a clear cross-sectional fracture. For the sintered hollow fibres, the clear cross-sectional fractures can be easily obtained by directly snapping the fibres. These membranes were then placed on a metal holder and sputtered with gold under vacuum. High-resolution images of the outside surfaces and the cross-section of the hollow-fibre membranes were taken at different magnifications. The surface roughness was determined using Atomic Force Microscopy (DI NanoScope Multimode). Gas permeation characteristics and gas-tight property of the membranes were measured using methods developed by Kong and Li [12] and Tan et al. [13], respectively. Purified nitrogen (BOC Gas) was chosen as the test gas. The sintered membranes with one end sealed were first glued onto a stainless steel sample holder with an epoxy resin (UKR-135 resin with UKH-136 hardener; UK Epoxy Resins, Lancashire, UK) and then assembled onto a test module (with known volume) with a high sensitivity pressure transducer (Model PX300-050GV; Omega Engineering Inc., Stamford, CT). For samples containing substantial pores, the nitrogen permeation fluxes were measured using a soap-bubble meter at different operating pressures. The data obtained were used for pore size distribution calculation using the gas permeation method developed by Kong and Li. [12] In the case of the samples being substantially dense, only a precise amount of nitrogen was fed into the test module. Therefore, the varying nitrogen pressures of the test module recorded at room temperature can be used to determine the gas-tight property. The details of the experimental setup and the permeation calculation can be found elsewhere. [13]

3.3 Results and discussion

3.3.1 Morphology of the YSZ hollow-fibre membranes

In this study, YSZ hollow-fibre membranes consisting of an asymmetric structure with a porous inner surface and an outer dense thin layer have been prepared. In order to achieve such a structure, control of suspension composition and spinning parameters is considered to be important. It has been reported that air gap, internal coagulant and humidity in the air gap are the main factors affecting fibre structures of polymeric membranes. [14–18] However, for ceramic membrane fabrication, the above factors were found to be also important, but to a lesser extent. [18] Therefore, in this study, the asymmetric structure of the YSZ membrane was achieved using the spinning conditions given by Liu et al. [19, 20] with considerable modifications in particle contents/type in starting suspension and sintering conditions. A total of three different starting suspensions were prepared as shown in Table 3.1. The starting suspension of S1 and S3 contain only one population sized particles, while the starting suspension of S2 contains two population sized particles where the total amount of the particles used is the same as S1, and the amount of large particles used is the same as S3. Figure 3.1 shows the SEM photographs of the asymmetric structure of the YSZ hollow-fibre membranes prepared from starting suspension S1.

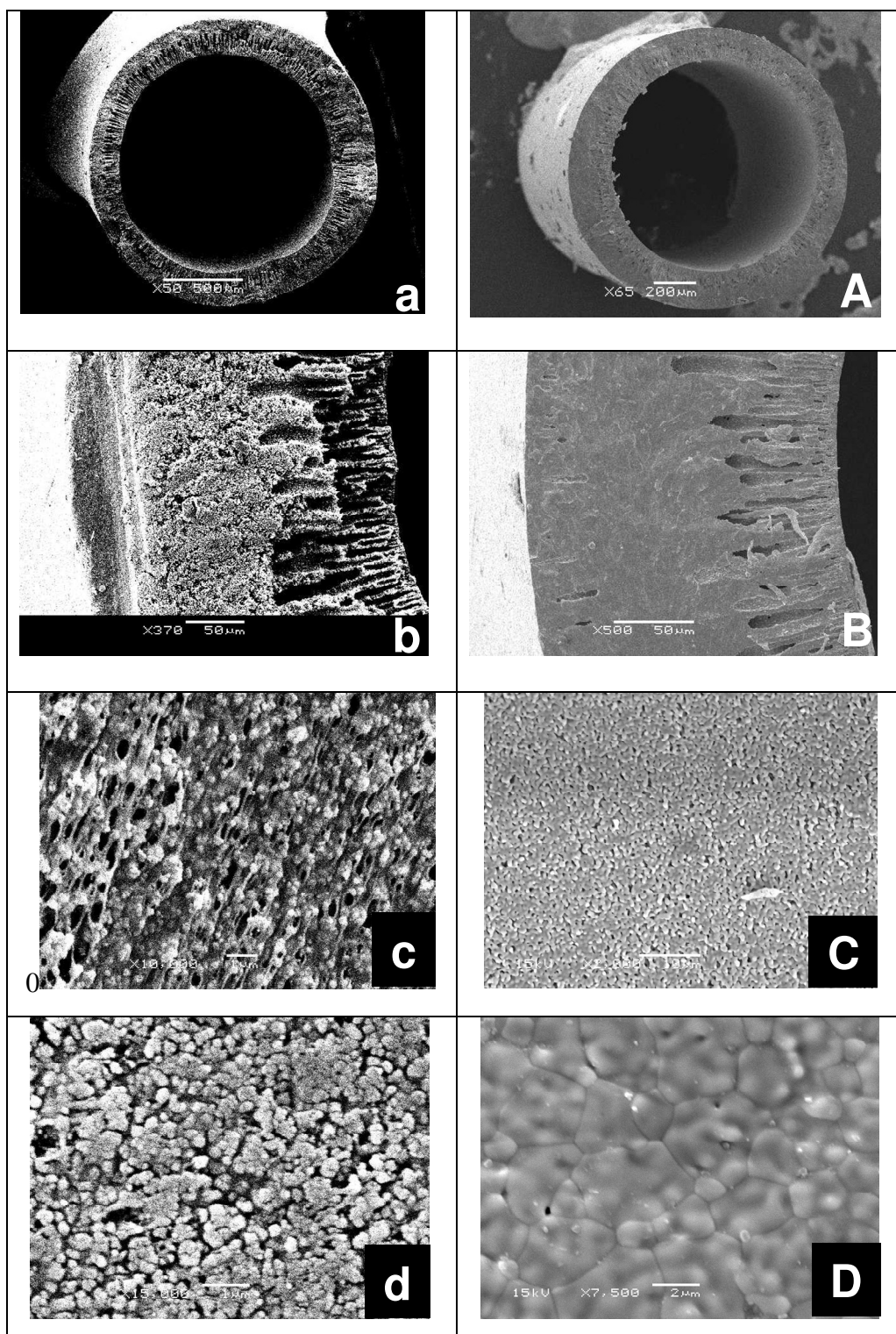


Figure 3.2 Structures of YSZ hollow-fibre membranes prepared using starting suspension of S1: (a-d: before sintering, A-D: after sintering at 1500 °C for 4 h; a-A, whole fibre; b-B, cross-section; c-C inter surface; d-D outer surface)

As can be seen from Figure 3.1(a and A), the outer and inner diameters (OD/ID) of the hollow-fibre precursor and sintered fibre were measured to be 2.0mm/1.2mm and 1.3mm/0.8mm, respectively. Figure 3.1(b and B, c and C, d and D) shows the cross-

sectional structures, inner surfaces and outer surfaces of precursor and sintered fibre, respectively. As can be seen, a finger-like structure is formed in the inner surface and is then gradually transformed to a denser sponge-like structure towards outer surface. Such a structure was formed due to the several factors such as viscous fingering phenomenon and movement of particles. In this study, during the spinning of the ceramic membrane precursors, pure water was used as the internal coagulant and was immediately in contact with the high viscous suspension. Therefore, the hydrodynamically unstable viscous fingering takes place, resulting in finger-like structures in the inner surface as long as the rate of viscous fingering is greater than that of phase inversion. Figure 3.1 also illustrates that the finger-like structure in outer surface of the hollow fibre is much suppressed. This is because during the spinning of the fibre precursors, an air gap (normally longer than 15 cm) was used so that the external surface of the nascent fibre experienced solvent evaporation and absorption of water moisture from air, both of which would induce the phase inversion of the polymer binder. Therefore, the viscous fingering may not be possible to establish, as solidification of the outer surface takes place before immersing the nascent fibre into the external coagulation bath. Figure 3.1 further illustrates that the asymmetric structure is generally maintained after high temperature sintering. Compared to the inner porous surface of the fibre as shown in Figure 3.1(C), Figure 3.1(D) depicts the outer surface of the sintered fibre, which is dense and smooth and consists of tightly connected grains with clear boundaries formed during sintering. The size of grains is in the range between 1 μm and 3 μm , which is grown in size compared to the initial particle size used in the starting suspension. Figure 3.2 illustrates a layered surface view of the sintered YSZ fibre.

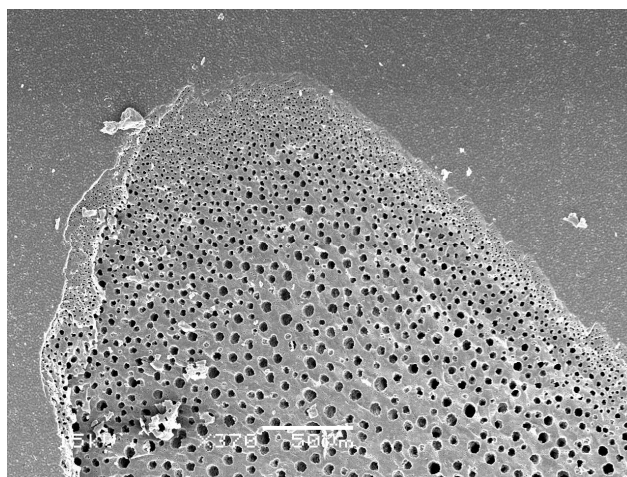


Figure 3.3 SEM micrograph of a layered surface of the YSZ hollow fibre (S1 sintered at 1500 °C for 4 h).

It can be seen that the dense/non-porous layer on the outer surface of the hollow fibre is gradually transformed to a sponge-like porous structure and then to a final finger-like macrovoid substrate to fibre lumen, further confirming that the asymmetric YSZ membrane can be prepared in one-step.

The effect of sintering conditions on the membrane surface morphology was further investigated. Figure 3.3 illustrates evolution of the surface morphologies at different sintering temperatures between 1000 °C and 1500 °C with the sintering times of 4 h and 8 h, respectively.

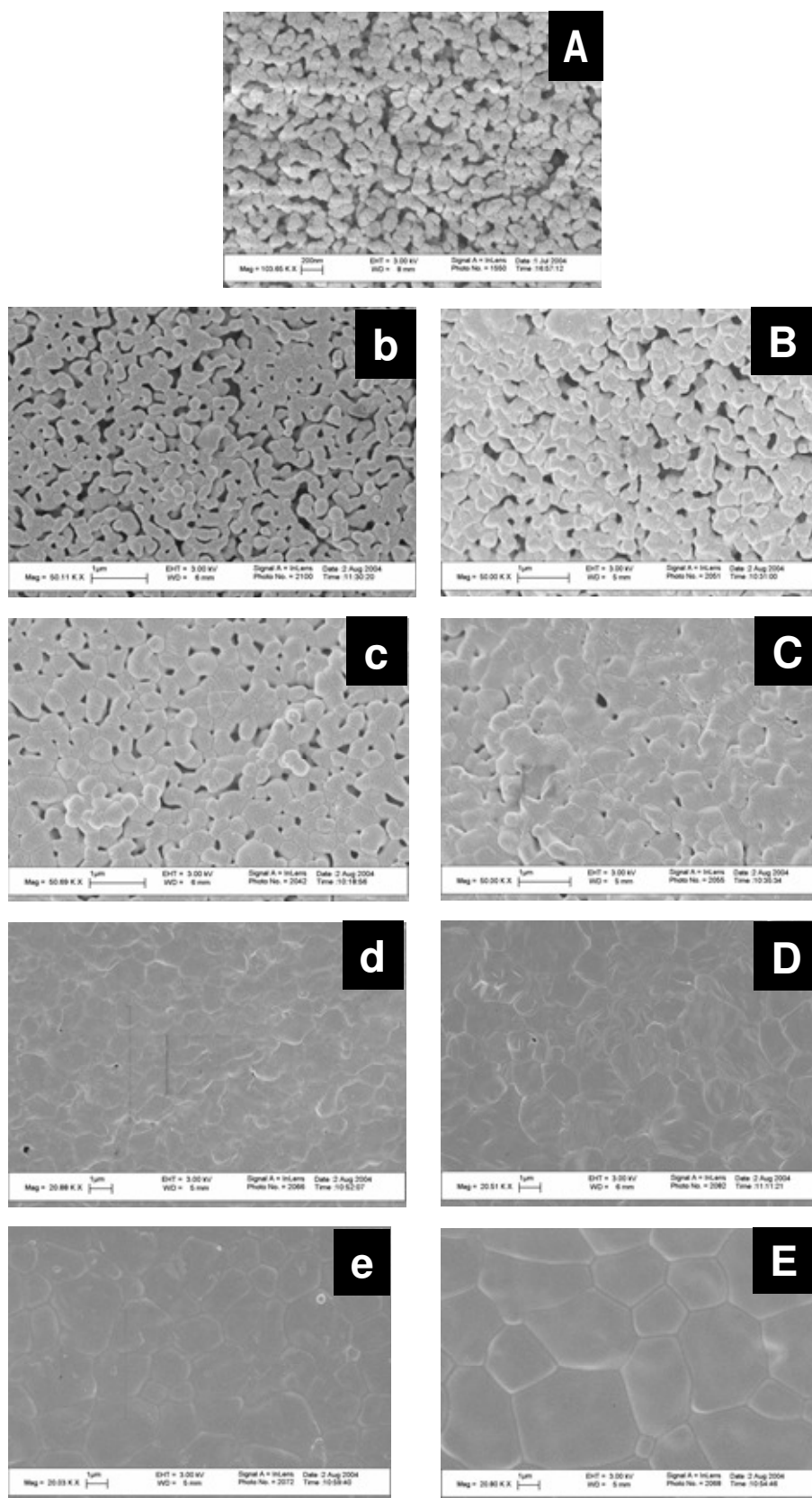


Figure 3.4 Surface morphology of the YSZ membranes prepared using S1 and sintered at different temperatures for 4 h (b-e) and 8 h (A-E), respectively; (A): 1000 °C, (b-B): 1200 °C, (c-C): 1300 °C, (d-D): 1400 °C and (e-E) 1500 °C

It can be seen that porosities of the membrane surface are reduced greatly when the sintering temperature is increased for both the sintering time of 4 h and 8 h. At the sintering temperature of 1000 °C, the membrane surface almost remains unchanged as the original morphology formed by the raw particles as shown in Figure 3.3(A). Obvious changes in the surface morphology take place at about 1200 °C, and the interconnected pores are observed from the membrane surface as shown in Figure 3.3(b and B) for both the sintering times of 4 h and 8 h. At sintering temperature of 1300 °C, the interconnected pores are still observed from the membrane surface as shown in Figure 3.3(c and C), although their porosities are much reduced compared to those sintered at 1200 °C. When the sintering temperature is increased to 1400 °C, the membrane surface becomes almost fully dense as shown in Figure 3.3(d and D). Further increasing the sintering temperature up to 1500 °C, no obvious pores can be observed, the grain size is increased considerably as shown in Figure 3.3(e and E). Compared to the membrane surfaces sintered at temperatures of 1200 °C and 1300 °C for 4 h (as shown in Figure 3.3(b and c)), the porosity of the membrane surfaces sintered at the same temperatures for 8 h are much smaller (as shown in Figure 3.3(B and C)). The above observation indicates that both sintering temperature and sintering duration play important roles for pore formation or elimination of the YSZ hollow-fibre membranes. The SEM photographs shown above provide useful information on the sintering behaviour of the prepared YSZ hollow-fibre membranes. Based on the particle packing principle, the voids (pores) formed between the particles can be reduced by filling the voids with smaller particles. [21] The effect of smaller particles on the surface morphology of the membranes was investigated using the starting suspension of S2 where 10% of 0.1 μm was replaced by 20 nm particles. SEM observation of the resultant membrane is given in Figure 3.4 together with the SEM of the membrane prepared from S3 at the identical sintering condition for comparison purpose.

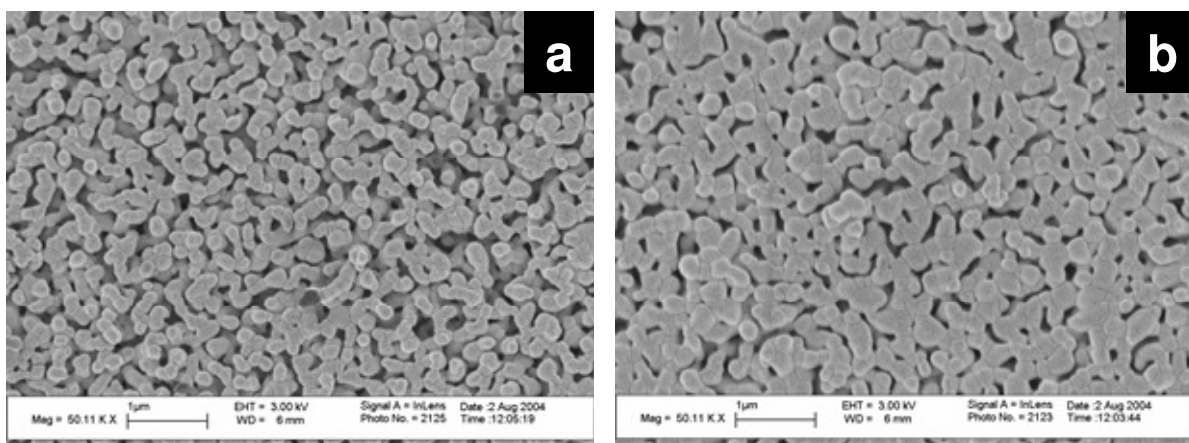
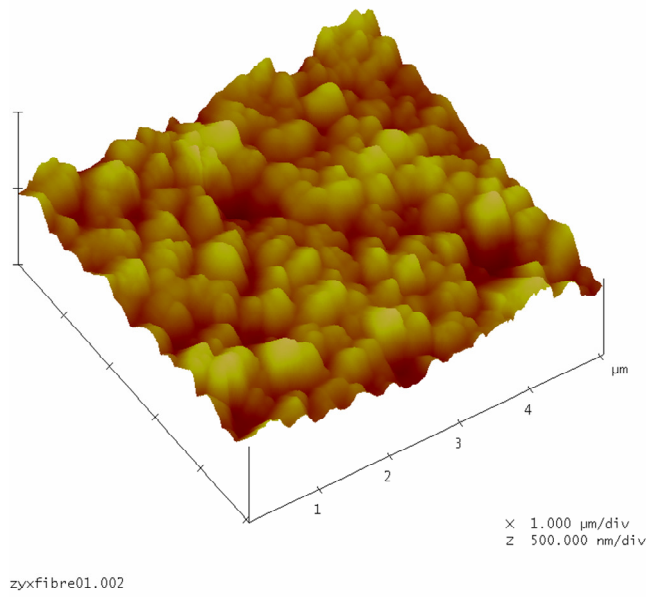
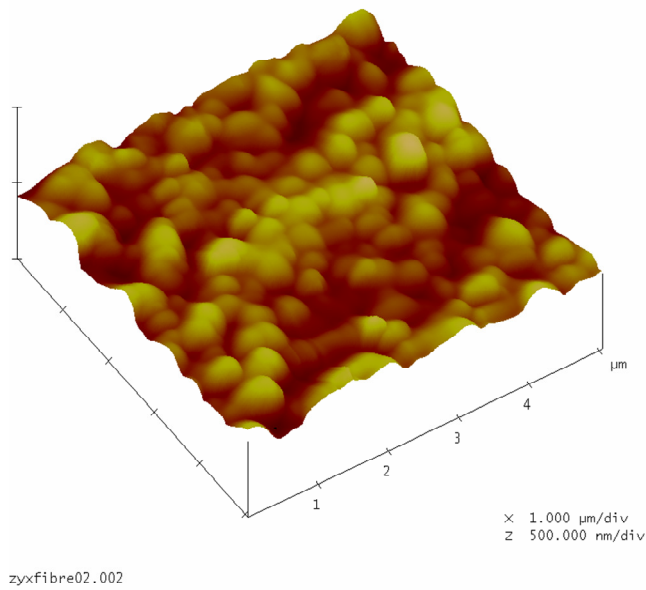


Figure 3.5 Surface morphology of the YSZ membranes sintered at 1200 °C and prepared from: (a) S3 and (b) S2

It can be seen that the membrane surface obtained using low powder contents of S3 (45% of 0.1 μm powders) and sintered at 1200 °C is still very porous (Figure 3.4(a)). However, the porosity of the YSZ hollow-fibre membrane is considerably reduced if a 10% of 20nm particles are added in the starting suspension as shown in Figure 3.4(b). It follows that addition of smaller particles would enhance the densification of the membrane, which would be particularly important if the prepared YSZ membrane is used as a membrane electrolyte for solid oxide fuel cells. Figure 3.5 shows the AFM images of the outer surface of the prepared YSZ hollow-fibre membranes, which are presented in 5 $\mu\text{m} \times 5 \mu\text{m}$ scanning area.



a



b

Figure 3.6 AFM images of the YSZ membranes: (a) S1 sintered at 1200 °C and (b) S1 sintered at 1300 °C

It can be seen that the surface of the membranes is not smooth but consists of a mass of peaks (bright region) and valleys (dark region). Roughness of the membranes, in terms of mean roughness, R_a and root mean square roughness, R_q , are obtained from the AFM images and are summarized in Table 3.2.

Table 3.2 Surface roughness data

Roughness (scan size = 5 μm $\times$ 5 μm)		
	R_a (nm)	R_q (nm)
1200 $^{\circ}\text{C}$	42.41	54.40
1300 $^{\circ}\text{C}$	34.06	41.88

Obviously, the membrane's roughness may reflect the surface porosity of the membrane because the valleys may probably be the membrane's pores on the surface.

3.3.2 Gas permeation characteristics of YSZ hollow-fibre membranes

A gas permeation test using purified nitrogen as a test gas was carried out in this study to determine the permeation characteristics of the YSZ hollow-fibre membrane prepared. Since the membranes prepared using the starting suspension of S3 are very porous and showed remarkable high gas permeance, only the effect of sintering temperature on the gas permeance for the membranes prepared using starting suspensions of S1 and S2 was studied and the results are illustrated in Figure 3.6.

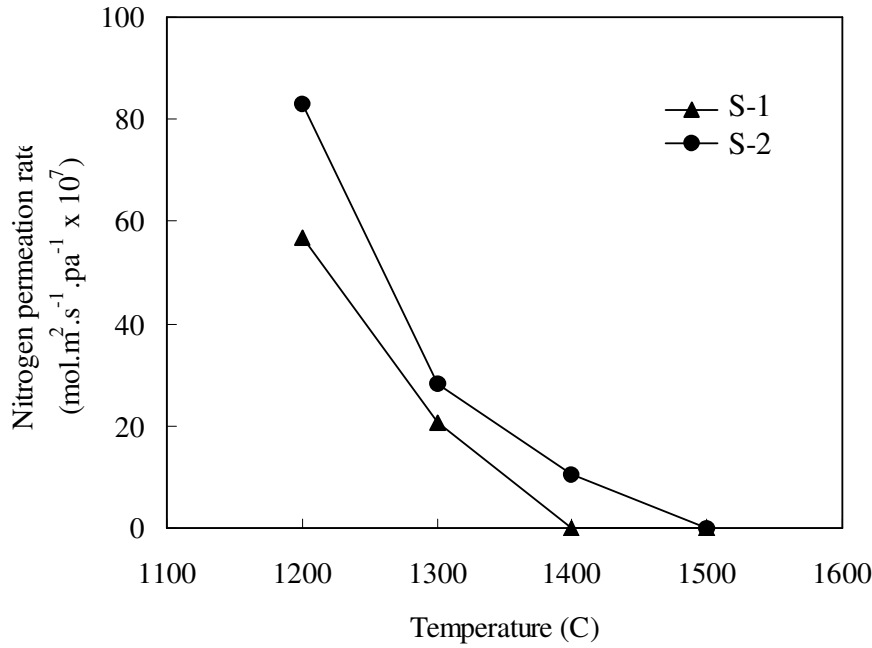


Figure 3.7 Gas permeance of the YSZ hollow-fibre membranes prepared using starting suspensions of S1 and S2 at different sintering temperatures for 8 h

As can be seen, the gas permeance for both membranes decreases as sintering temperature is increased. The gastight property for the membrane prepared using S1 could be achieved at sintering temperature of 1400 °C whereas the membrane prepared using S2 still showed a nitrogen permeance of $10.6 \times 10^{-7} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ at same sintering condition and could not be gas-tight unless the sintering temperature is increased to 1500 °C. It should be noted that the gas-tight property for the membrane of S1 was further determined using a method developed by Tan et al. [13] The obtained nitrogen permeance is less than $2.0 \times 10^{-10} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$, further confirming that the membrane is non-porous and is gas-tight. It should be noted that although similar result to the above was also obtained by Tan et al. [11], it is contrary to the analysis conducted by Lu [22] who showed theoretically that the porosity (hence permeance) of a ceramic powder compact reduces when smaller particles are used alone for preparation of the powder compact. In general, addition of smaller particles would enhance the densification i.e. reduce the volumetric pores. However, it may not be true for the surface pores (through pores for permeation). In this study, an immersion induced phase-inversion process was employed for spinning of the hollow fibre. As pore formers were added into the spinning suspension, asymmetric

structure and surface pores of the fibre precursor were formed during the coagulation process and were altered after the sintering. In view of the complicity of the combined spinning and sintering processes, the relationship between the particle size and the structure of the final resultant membrane remains unclear and needs to be further explored. The presence of the 20 nm particles, however, enhances significantly the mechanical strength of the hollow fibres as shown by Liu et al. [19]

Based on the gas permeation data plotted in Figure 3.6, the membranes sintered at temperature less than 1400 °C are porous. Thus, the data were used to calculate the pore size distribution of the membranes using a method developed by Kong and Li. [12] The purpose of this analysis is obviously to investigate the behaviour of surface porosity in the membranes, as it is impossible to obtain membranes with absolutely uniform pore size using the method described above. In fact, the membrane pore size varies according to a pore size distribution function. Comparison between S1 and S2 at sintering temperatures of 1200 °C and 1400 °C for 4 h was carried out. The behaviours of the pore size distribution are shown in Figure 3.7 where the x-axis represents the membrane pore radius, r , (μm) and the y-axis represents the log-normal distribution function, $g(r)$ as follow: [12]

$$g(r) = \frac{1}{r\sqrt{2\pi}} [\ln(1 + \sigma^2)]^{-0.5} \exp\left[-\frac{(\ln(r/r_m)(1 + \sigma^2)^{0.5})^2}{2\ln(1 + \sigma^2)}\right]$$

where r_m is the mean pore radius; and σ is the dimensionless standard deviation of the membrane pore size. It can be seen that at sintering temperature of 1200 °C, both S1 and S2 show similar distribution of pore size, where the mean pore radius fall in 0.07 μm and 0.03 μm , respectively. When the sintering temperature was increased to 1400 °C, the membrane from S1 achieved gas-tight, suggesting that surface pores were eliminated at this temperature as shown in Figure 3.6, while for the membrane prepared from S2 still showed a nitrogen permeance of $10.6 \times 10^{-7} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ with a narrow distribution as shown in Figure 3.7 compared to that sintered at 1200 °C, although the mean pore size remained unchanged at 0.03 μm .

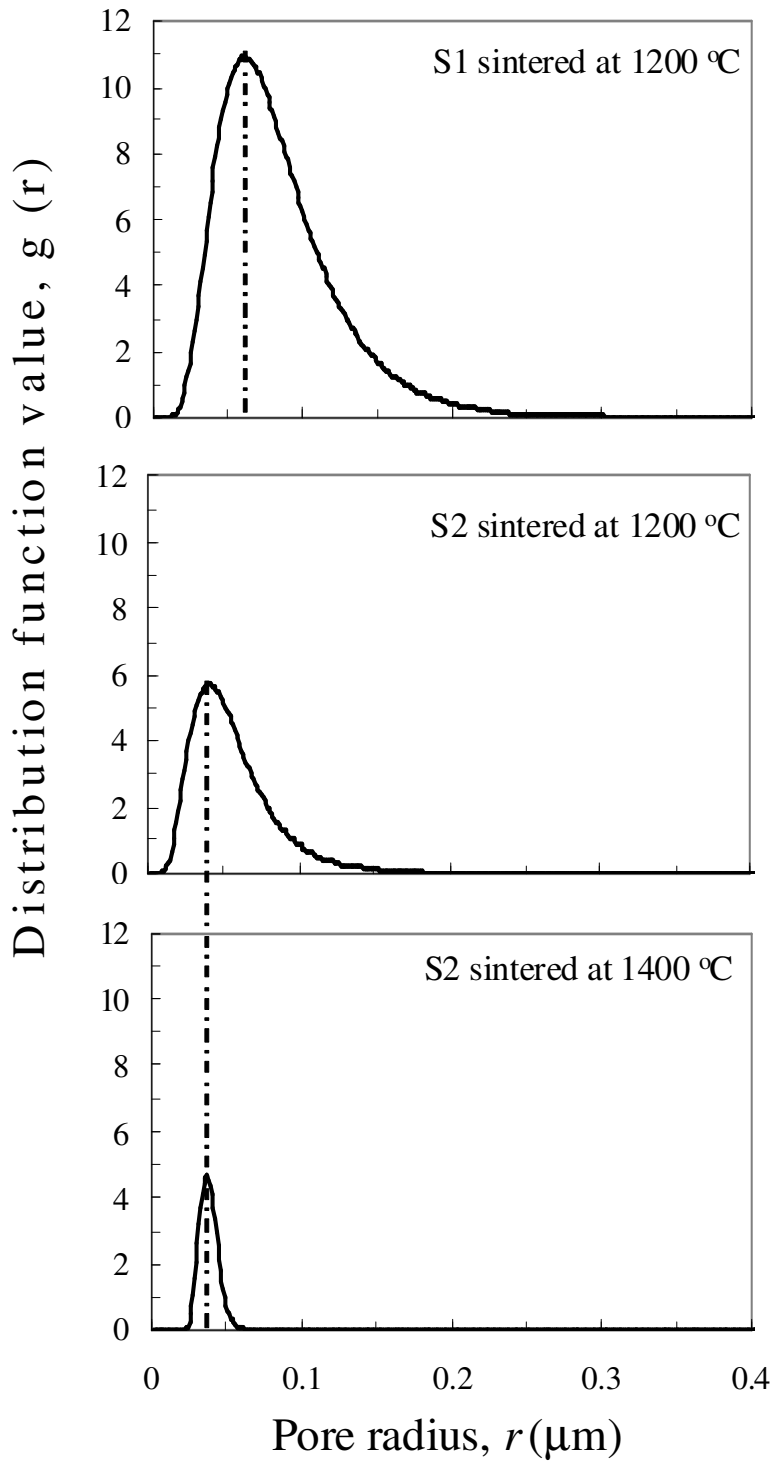


Figure 3.8 Pore size distributions of S1 and S2; sintering time: 4 h

It should be noted that the results on the narrow distribution with increased sintering temperature are uncommon, as the reduction in porosity should normally be at the expense of smaller pores. The reason for such contrary results may be due to the fact that the pores measured using the gas permeation technique are through pores only.

Large pores growing due to the increase of sintering temperatures may be dead-end pores and cannot be detected by the gas permeation technique. Above gas permeation analysis suggests that both porous and non-porous YSZ hollow-fibre membranes can be prepared, depending on the sintering conditions. Pore sizes of the YSZ membrane prepared fall into the pore size range of ultrafiltration membrane. However, the surface porosities of the membranes prepared from S2 and sintered at 1200 °C and 1400 °C are around 5000 m⁻¹ and 300 m⁻¹, respectively. The former is comparable to the polymeric PVDF membranes, while the latter is an order of the magnitude smaller. [23]

3.4 Conclusions

Ceramic hollow-fibre membranes which have an asymmetric structure have been prepared in one step by spinning a suspension containing distributed sized particles through a conventional tube-in-orifice spinneret. It is believed that the asymmetric structure is formed because of the viscous fingering and different rates of particle movement during the phase inversion. The results shown in this study suggest that a good control of particle size distribution in the suspension and exchange rates of the solvent and nonsolvent may tailor the membrane with an asymmetric structure, which can only be prepared in multiple steps if conventional techniques are used.

Gas permeation analyses suggest that both porous and nonporous YSZ hollow-fibre membranes can be prepared depending on the sintering conditions. Pore sizes of the YSZ porous membranes prepared fall into the pore size range of ultrafiltration membranes. However, the surface porosities of the membranes sintered at 1200 °C and 1400 °C are around 5000 m⁻¹ and 300 m⁻¹, respectively. The former is comparable to the polymeric PVDF membranes, while the latter is an order of the magnitude smaller. [23]

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Chapter 4 Preparation and characterization of a robust and hydrophobic ceramic membrane via an improved surface grafting technique

Abstract

Studies have shown that hydrophilic surfaces of ceramic membranes can be modified to be hydrophobic using a grafting method. In this study, a robust and hydrophobic ceramic hollow-fibre membrane was developed by introducing a pretreatment technique, followed by a grafting method. The contact angle of the grafted membranes using the pretreatment technique was approximately 140° , indicating that the hydrophilic membrane surfaces were successfully modified to be hydrophobic. The mean roughness and the root roughness of grafted membranes decreased from 41 to 27.6 nm and from 53.4 to 33.6 nm, respectively, indicating that the membrane was covered by a grafted layer. The mechanical strength of the membrane was retained after the grafting process, and the grafted membrane was found to be thermally stable up to 270°C and chemically stable in hexane for 100 h.

4.1 Introduction

Ceramic membranes are well-known for their superior thermal and chemical stability. Over the past decade, a considerable number of studies have been conducted on ceramic hollow-fibre membranes because of their high surface areas per unit volume (up to $9000\text{ m}^2\text{ m}^{-3}$) compared to those of plate-and-frame or tubular membrane configurations, which are in the range of $30\text{-}500\text{ m}^2\text{ m}^{-3}$. [1] Also, it was shown that the cost of ceramic hollow-fibre modules for use as membrane reactors is 10 times less than that of tubular and multichannel tubular ceramic membranes. [2] Ceramic membranes have been widely used in applications such as gas separation, [3, 4] membrane reactors, [5, 6] oil/water separation, [7, 8] and wastewater treatment, [9, 10] some of which rely highly on the hydrophilic nature of the ceramic membranes. Ceramic membranes have limited use in nonpolar solvent separation and in membrane contactors for aqueous media because of the hydrophilic nature of most ceramic

membrane materials. Therefore, it is important to develop hydrophobic ceramic membranes to develop the applications mentioned above.

Chemical grafting techniques are commonly used to increase the hydrophobicity of ceramic membranes. [11, 12] Several compounds such as perfluorodecyltriethoxysilane, fluoroalkylsilanes, and polyvinylpyrrolidone are widely used in the grafting process. [11-13] These grafting components have both a hydrolysable end unit and a hydrophobic tail. The hydrolyzable groups chemically bond with hydroxyl groups (OH^-) on the ceramic membrane surface, whereas the hydrophobic tails increase the hydrophobicity of the ceramic membrane surface. The grafting technology is highly dependent on the amount of hydroxyl groups on the ceramic membrane surface. However, the hydroxyl groups in ceramic materials (most metal oxides) are easily suppressed during heat treatment, which is a necessary step for the consolidation of the membrane mechanical strength in most ceramic membrane fabrications. Conventional technologies such as application of an additional thin hydrophilic ceramic layer on the membrane surface or direct hydroxyl-ion bombardment have been used to increase the concentration of OH^- groups on the membrane surface before the grafting process. [14-18]

However, these technologies involve either extra thermal energy or a complex apparatus. Therefore, it is necessary to find a simple, fast, and efficient technology to restore the OH^- groups on the membrane surface. Some reports have shown that the number of OH^- groups can be increased by controlling the pH value of the yttria stabilized zirconia (YSZ) particle suspension, which also affects the viscosity and stability of the YSZ suspension. [19, 20] Kang et al. unexpectedly found that the surface charge of a zirconia membrane changed to a more negative value after the membrane was rinsed in an alkaline solution. [21] Therefore, it is believed that the pH value is an important factor in restoring hydroxyl groups to the membrane surface.

Several studies have focused on the hydroxyl groups of partially stabilized zirconia because of its superior mechanical properties, which endow it with great potential in membrane technology. [21-23] De Ridder et al. and Morterra et al. have reported that the OH^- groups of YSZ disks mainly come from adsorbed water. [24, 25] Zhu et al. also observed the presence of hydroxyl groups on YSZ powders after exposure to

water vapor for 30 min. [26] Water vapor could be another important factor in controlling the concentration of hydroxyl groups on the membrane surface. The aim of this study was to develop a robust and hydrophobic ceramic membrane in the hollow-fibre configuration. YSZ was selected as the membrane material because of its high mechanical strength [27] and competitive price, [28] although it has mostly been applied in electrochemical applications such as solid oxide fuel cells, [29] oxygen sensors, [30] and high-temperature pH sensors. [31] Because of the inherent surface properties of YSZ, which make it difficult to restore OH⁻ groups, a pretreatment technique, such as alkaline or steam pretreatment, was introduced to enhance the amount of OH⁻ groups on the surface of the YSZ ceramic membrane for further chemical grafting processes. After the grafting process, both the surface and permeation properties, including contact angle, solvent permeability, surface roughness, and pore size distribution, and structural properties such as membrane morphologies and mechanical strengths were tested. The grafted YSZ membrane was found to be thermally stable up to 270 °C and chemically stable in hexane for 100 h.

4.2 Experimental Section

4.2.1 Materials

Commercially available 8 mol % yttria stabilized zirconia (8YSZ) powders with mean particle diameters of 0.25 μm ($d_{50} = 0.25 \mu\text{m}$; surface area = 8-13 $\text{m}^2 \text{g}^{-1}$) and 10 nm ($d_{50} = 10 \text{ nm}$; surface area = 154 $\text{m}^2 \text{g}^{-1}$) purchased from NexTech Materials Ltd. (Lewis Center, OH) were used for preparation of YSZ ceramic hollow-fibre membranes. Polyethersulfone (PESf) (Radel A300, AMECO Performance, Greenville, SC), 1-methyl-2-pyrrolidinone (NMP) (HPLC grade, Sigma-Aldrich, St. Louis, MO), and Solsperse 3000 (Noveon Inc., Cleveland, OH) were used as the binder, the solvent, and the additive, respectively. Fluoroalkylsilanes (FASs) (Lancaster Synthesis, Windham, NH) and hexane (HPLC grade, Sigma-Aldrich) were used for the surface grafting process.

4.2.2 Membrane preparation

The immersion-induced phase inversion and sintering technique was employed in preparing the YSZ hollow-fibre membranes. The detailed procedures were described elsewhere. [32, 33] A spinneret with orifice outer diameter (o.d.) and inner diameter (i.d.) of 2.0 and 0.7 mm, respectively, was used to obtain the hollow-fibre precursors. The spinning conditions and composition of the suspension for the preparation of the YSZ hollow-fibre precursors are given in Table 4.1.

Table 4.1 Compositions and spinning conditions of the YSZ hollow-fibre membrane precursors

Compositions of the Starting Suspension (wt %)	
YSZ powder ($D_{50} = 0.25\mu\text{m}$) (NexTech Materials Ltd., Ohio)	62.7%
YSZ powder ($D_{50} = 10\text{nm}$) (NexTech Materials Ltd., Ohio)	3.3%
polyethersulfone (PESf) (Radel A300, Ameco Performance, USA)	6.6%
additive (Solsperse 3000, Noveon Inc., Ohio)	0.12%
NMP (HPLC grade, Sigma-Aldrich, UK)	27.28%
Conditions of Spinning Process	
internal coagulant	deionized water
internal coagulant temperature ($^{\circ}\text{C}$)	20
injection rate of internal coagulant (ml min^{-1})	7-10
external coagulant	tape water
external coagulant temperature ($^{\circ}\text{C}$)	20
air gap (cm)	40
nitrogen pressure (psi)	3-5

The final YSZ hollow-fibre membranes were produced by heat treatment of the precursors in a CARBOLITE furnace with air. The furnace temperature was first increased at a rate of $2^{\circ}\text{C min}^{-1}$ to 600°C , where the thermolysis (i.e., removal of the polymer binder) was carried out for 2 h. The temperature was then further increased to $1300\text{-}1600^{\circ}\text{C}$ at $5^{\circ}\text{C min}^{-1}$ and was held for 3 h for the final sintering. Finally, cooling was carried out to room temperature at a rate of $5^{\circ}\text{C min}^{-1}$.

4.2.3 Surface modification

YSZ hollow fibres with and without pretreatment were used for surface modification. Both steam pretreatment and alkaline methods were employed. For the steam pretreatment, sintered YSZ membranes that were 10 cm in length and had both ends sealed were placed in an oven that was maintained at 100 °C with 100% relative humidity for 24 h. After being cooled and dried in air, the membranes were ready for surface modification. In the alkaline pretreatment, the sintered YSZ hollow fibres that were 10 cm in length were sealed off at both ends and then immersed into pretreatment solutions of different pH values. The pretreated fibres were then dried in an oven at 100 °C for 24 h. After being cooled, the fibres pretreated by the alkaline method were ready for surface modification. The pH value is an important factor in alkaline pretreatment. A higher concentration of alkaline solution could provide more OH⁻ groups for membrane surfaces and improve the grafted amount of FASs. However, ceramic membranes usually cannot withstand highly alkaline solutions. Shinj et al. observed that an alumina membrane was corroded in a 10 wt % sodium hydroxide solution. [34] In their study, a zirconia layer was coated on the alumina membrane to enhance the corrosion resistance of the alumina membrane. They found that the alkaline corrosion resistance was efficiently increased with the thickness of zirconia layer. Shojai et al. reported the chemical stability of YSZ membranes in acid and alkaline solutions. [35] They observed that yttrium and zirconium would dissolve in acidic solution (pH 2) at room temperature for 79 days. The dissolutions of yttrium and zirconium were more obvious as the temperature of the acid solution was increased to 80 °C. However, the YSZ membranes were chemically stable in alkaline solution (pH < 12) at 80 °C for 34 days. Therefore, in this work, the pH range from 7 to 11 was chosen to study in alkaline pretreatment effects.

The surface modification procedure involves the following steps: (i) rinsing sintered or pretreated YSZ fibres with hexane (Sigma-Aldrich) solution in an ultrasonic bath, (ii) drying in air, (iii) grafting of FASs on the membrane surface at 40 °C in a solution containing 0.01 M FASs in hexane, (iv) removing YSZ fibres from the grafting solution, (v) rinsing grafted YSZ fibres with hexane in an ultrasonic bath, and (vi) drying at 100 °C for 24 h. After cooling, the grafted fibres were ready for further characterization.

4.2.4 Membrane characterization

The following membrane characterization techniques were used: contact angle measurement, permeability test, morphological analysis, surface analysis, bubble-point test, mechanical strength measurement, thermogravimetric analysis (TGA), and solvent stability test.

Contact angle measurements were used to evaluate the effects of the surface modification on the hydrophilic/hydrophobic properties of the membranes. These measurements were performed using the Wilhelmy technique, which is currently recommended for hollow-fibre membranes. [11] The open ends of the hollow fibres were sealed off with epoxy resins and hung on the microbalance in the tensiometer (Kruss K100). Then, they were gradually immersed in quiescent testing liquid, which was deionized water in this case. The rate of immersion was controlled at 6 mm min⁻¹, and all measurements were made at 20 °C. The contact angles were calculated from the forces acting on the fibre surface, the wetting length, and the known liquid-vapor surface tension. The permeation tests were carried out with a single liquid feed system at room temperature. The feed solution was circulated into the shell side of the membrane using a gear pump (Michael Smith Engineering, GC-M23 series), and the operating pressure was recorded using a pressure gauge (Keller, Mano gauge). After a steady-state flux was achieved, permeation data were collected at 2 bar for nongrafted and grafted YSZ hollow-fibre membranes; the calculated permeability values are reported in Table 4.2.

Table 4.2 Surface and permeation characteristics of non-grafted and grafted YSZ hollow-fibre membranes

Sample	Water permeation (Lm ⁻² h ⁻¹ bar ⁻¹)	Hexane permeation (Lm ⁻² h ⁻¹ bar ⁻¹)	Roughness (scan size = 2µm × 2 µm)		Minimum bubble point pressure (bar)	Maximum pore radius (µm)
			R _a ^a (nm)	R _q ^b (nm)		
Before grafting	10.18	0	41.0	53.4	9.8	0.15
After grafting ^c	0	38.17	27.6	33.6	9.0	0.10

^a Mean roughness. ^b Square root roughness. ^c With an alkaline pretreatment (pH 11) for 8 h.

The morphologies of YSZ hollow-fibre membranes were studied using scanning electron microscopy (SEM, JEOL JSM-5610LV, Tokyo, Japan). The YSZ hollow-fibre precursor was immersed in liquid nitrogen for around 5 min to achieve a clear cross-sectional fracture. For sintered YSZ hollow-fibre membranes, a clear cross-sectional fracture was obtained by directly breaking the fibres.

Surface analysis was carried out using an atomic force microscope equipped with a J scanner and a NanoScope IV controller (Veeco, Cambridge, U.K.). Surface height and roughness were obtained from atomic force microscope images by tip scanning. In this study, the scan size was $2\ \mu\text{m} \times 2\ \mu\text{m}$, with a resolution of 512×512 points. The maximum pore size and pore size distribution (PSD) of YSZ hollow-fibre membrane were measured by the bubble-point method according to standard method ASTM F316-80. [36] The membrane to be tested was first immersed in a 50:50 (vol. %) mixture of hexane and deionized water. After 15 min, deionized water was used to gradually displace hexane to wet the membrane. The three-point bending test was used to determine the mechanical strength of the YSZ hollow-fibre membranes. A tensile tester (Instron Model 5544) with a load cell of 1 kN was used for this purpose. The membranes were fixed to a 30-mm-long sample holder and tested to the breaking point. The equation for the bending strength (σ_F) calculation is [37]

$$\sigma_F = \frac{8FLD}{\pi(D^4 - d_i^4)}$$

where F is the measured force at which fracture occurred and L , D , and d_i are the length, outside diameter, and inside diameter of the hollow fibres, respectively.

4.2.5 Thermal and chemical stability tests

Thermal stability was examined using a thermogravimetric analyzer (TA Instruments, Q500). The membranes were snapped into small pieces and placed in a sample holder. The sample holder was then hoisted on a microbalance and heated to $800\ ^\circ\text{C}$ in a small isolation chamber under an air flow rate of $60\ \text{ml min}^{-1}$. Any weight loss during the heating process was automatically recorded by the analyzer. To test the chemical stability, the grafted membranes were immersed into a hexane bath that was circulated

by a peristaltic pump (Watson-Marlow Bredel, 505U) providing a tangential velocity at the membrane surface of around 13.5 cm min^{-1} . The membranes were tested for 100 h, rinsed with deionized water, and dried in an oven at 100°C overnight. Eventually, the membranes were characterized by contact angle measurements.

4.3 Results and discussion

4.3.1 Membrane hydrophobicity

Contact angle measurements have been widely used to identify surface characteristics. [11, 12, 38] It has been suggested that a contact angle of 90° could be used as a criterion for distinguishing between hydrophobic and hydrophilic surfaces. The surface is considered to be hydrophobic if the contact angle is higher than 90° . Figure 4.1 shows the contact angles of alkaline-pretreated YSZ membranes at different pH values.

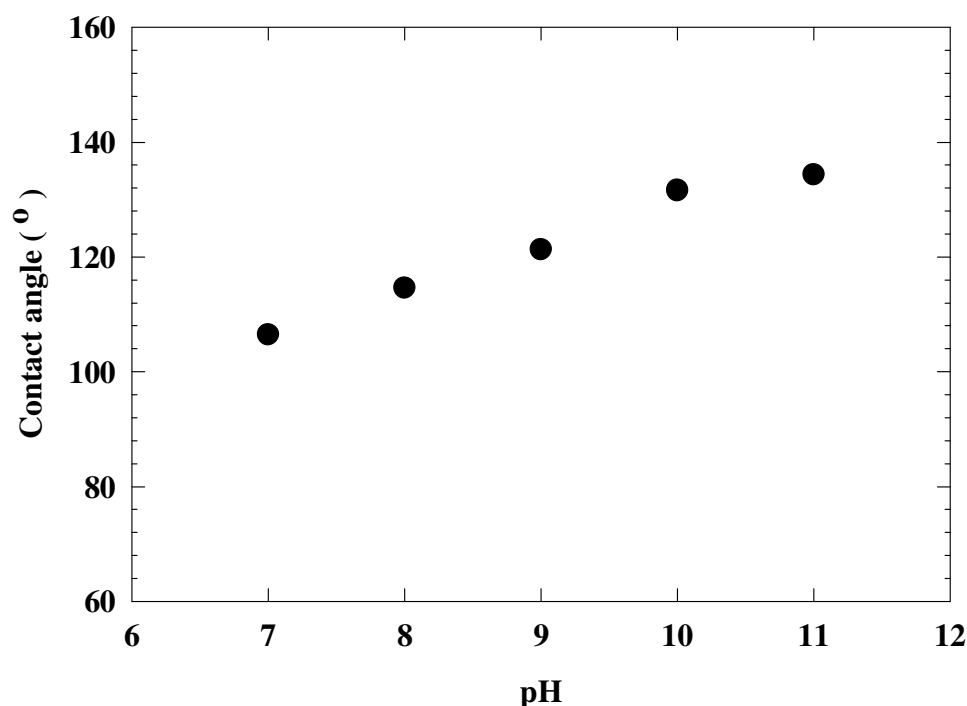


Figure 4.1 Effect of pH on the contact angle of the grafted YSZ membranes obtained using an alkaline pretreatment (grafting time = 8 h)

It can be seen that the contact angle of the grafted YSZ membranes increased as the pH of the alkaline solution increased. The contact angle levelled off at about 140°

when the pH value had increased to 11, indicating that the alkaline solution at this pH value can efficiently restore all of the OH⁻ groups on the YSZ membrane for surface modification. Therefore, alkaline pretreatment at pH 11 was employed in subsequent studies in this work. The effects of grafting time on the contact angles of various grafted YSZ membranes are depicted in Figure 4.2.

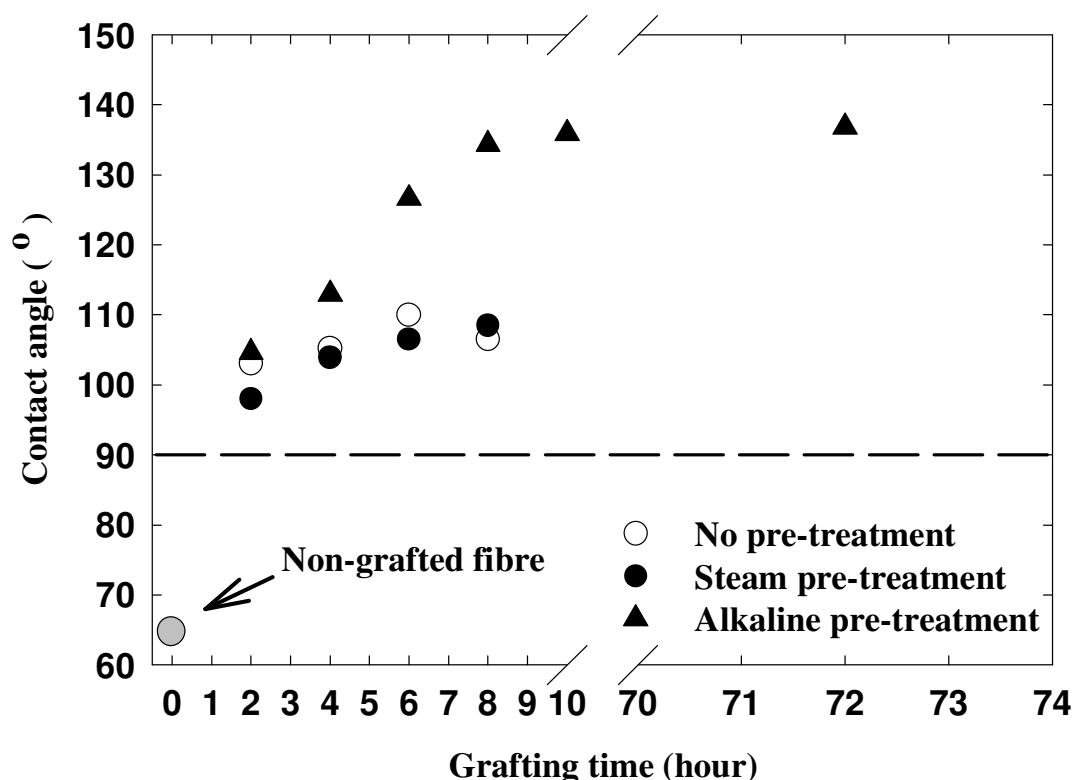


Figure 4.2 Effect of grafting time on the contact angles of various grafted YSZ membranes (grafting temperature = 40 °C).

The contact angle of a nongrafted YSZ membrane is 64.6°, indicating that it is hydrophilic and likely to absorb water. After grafting, the contact angles of the YSZ membranes without pretreatment are in the range between 100° and 110°. Although these contact angles are considered to be hydrophobic and show competitive hydrophobicities when compared with hydrophobic membranes grafted onto a glass substrate, [39] they are not high enough for some applications that might require contact angles in the range between 120° and 140°. [40] The lower contact angles of grafted YSZ hollow-fibre membranes without pretreatment resulted from the variation in the membrane surface chemistry during the sintering process at temperatures between 500 and 800 °C. [41, 42] In this temperature range, the hydroxyl groups (OH⁻)

can be suppressed from the YSZ surface. The lower number of OH⁻ groups on the membrane surface reduces the amount of FASs that can be grafted. To increase the amount of grafted material, it is very important to restore the OH⁻ groups before grafting.

The contact angles of YSZ membranes after the alkaline pretreatment (pH 11) are in the range of 100°-140° after grafting for 72 h. In fact, the contact angle of about 140° was reached after grafting for only 8 h. These high contact angles resulted from greater amounts of FASs grafted on the membrane surface, indicating that the alkaline pretreatment can efficiently restore the OH⁻ groups on the membrane surface and allow more coupling reactions with FASs. The presence of FAS molecules effectively changed the membrane surface property from hydrophilic to hydrophobic. The hydrophobicity of grafted YSZ membrane can also be observed from the permeability data for hexane reported in Table 4.2. It can be seen that the grafted membrane shows a high permeability for hexane, whereas permeability is not observed for water. This result corresponds with the contact angle results, indicating that the surface has been successfully changed to hydrophobic.

Figure 4.2 also shows that the contact angles of the grafted YSZ membranes after steam pretreatment gradually increased and then remained steady at about 105° after grafting for about 8 h. It can be seen that the trend of increasing contact angles is similar to that without pretreatment. The hydrophobicity restored by the steam pretreatment method is most likely physically adsorbed, so that it can be washed during rinsing with hexane. The results from Figure 4.2 suggest that the alkaline pretreatment is most effective in restoring the OH⁻ groups. Therefore, in the following sections, all of the grafted membranes used were prepared through the alkaline pretreatment (pH 11) with a grafting time of 8 h.

4.3.2 Membrane morphology and surface roughness

The morphological transformation between the YSZ precursor and the sintered YSZ membrane is shown in Figure 4.3.

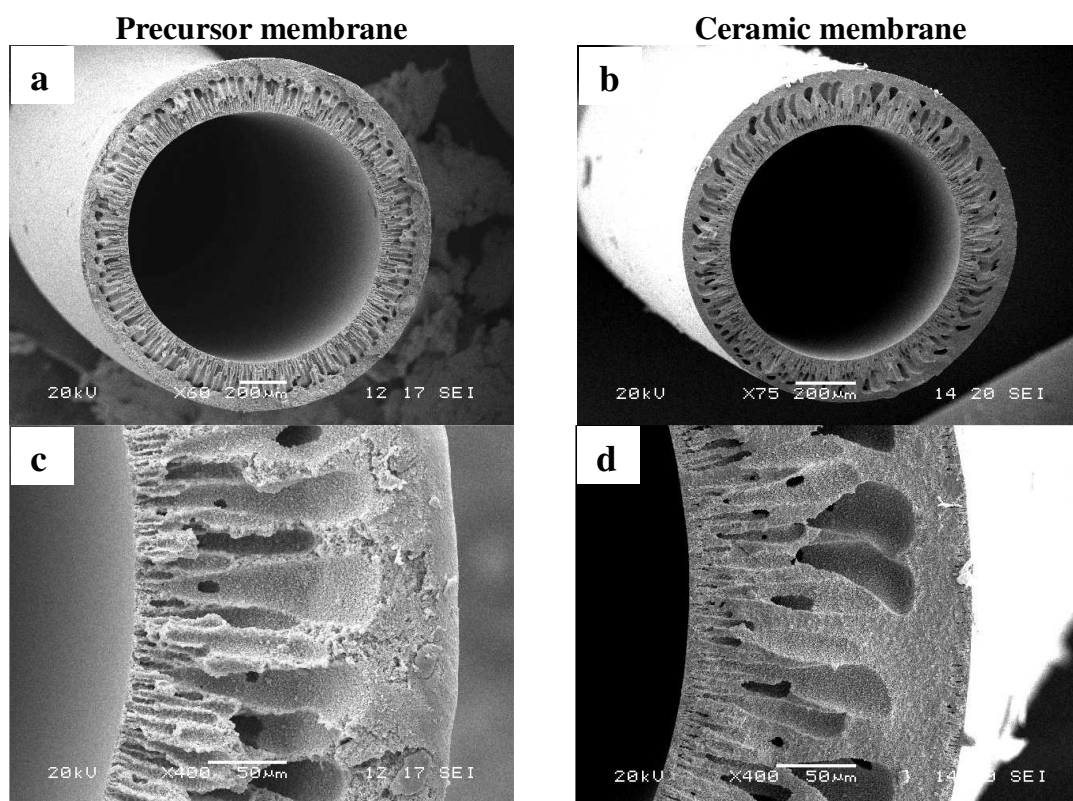


Figure 4.3 SEM images of YSZ hollow-fibre precursors and sintered YSZ hollow-fibre membranes (1300 °C, 3 h)

As can be seen from Figure 4.3 (a, b) the values of o.d./i.d. for the YSZ precursor and sintered YSZ membrane were measured to be 1.5/1.1 mm and 1.1/0.7 mm, respectively. The shrinkage of the YSZ membrane was caused by the removal of the polymer binder, solvent, and additive and the rearrangement of the YSZ particles during the sintering process. Figure 4.3 (c, d) shows the cross-sectional structures of the YSZ precursor and sintered YSZ membrane, respectively. As can be seen in Figure 4.3c, a fingerlike structure developed near the inner wall, and a spongelike structure formed near the outer wall. Such an asymmetric structure is attributed to several factors such as the viscous fingering phenomenon and the movement of particles. In this study, water was used as the internal coagulant. When it was in contact with the highly viscous YSZ suspension, the hydrodynamically unstable viscous fingering took place. As long as the rate of the viscous fingering is higher than the rate of phase inversion of the polymer binder, fingerlike structures will occur. Thus, the fingerlike structures developed in the fibre inner surface. The viscous fingering was not established in the outer surface. This is because a long air gap (40 cm) was used in this study. Such a long air gap facilitates solvent evaporation as well as absorption of water moisture from the air on the outer surface of the nascent YSZ

fibre, resulting in a dramatic increase in suspension viscosity or even a phase inversion on the outer surface before immersion of the nascent YSZ fibre into the external coagulation bath. Therefore, the spongelike structure the near outer wall formed, as the rate of inversion was greater than the rate of viscous fingering. The details of asymmetric ceramic hollow-fibre formation can be found elsewhere. [43] It should be noted that the dimensions and amounts of fingerlike macrovoids both decreased after sintering, as shown in Figure 4.3d. However, the asymmetric structure of the YSZ membrane was generally maintained after a high temperature heat treatment.

Figure 4.4 shows the outer surfaces of nongrafted and grafted YSZ ceramic hollow-fibre membranes.

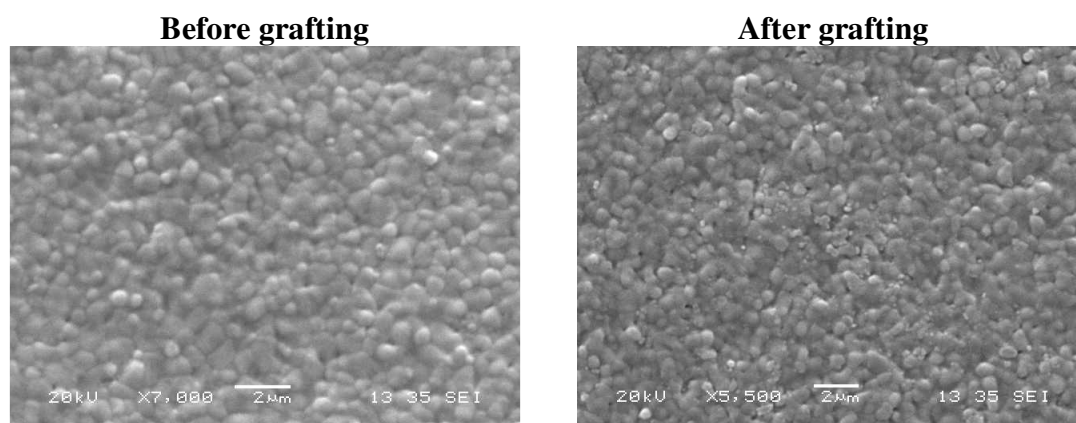
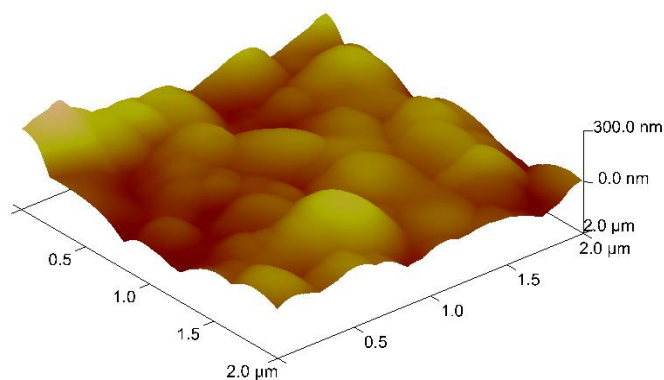


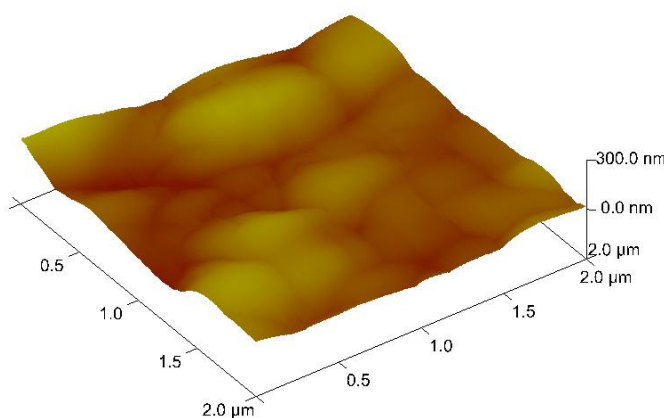
Figure 4.4 SEM images of the outer surfaces of nongrafted and grafted YSZ ceramic hollow-fibre membranes (1300 °C, 3 h)

It can be seen that there is no clear difference between the nongrafted and grafted YSZ varieties. The grafted FAS molecules were most likely bound to the YSZ membrane surface but could not polymerize to form an observable layer. Therefore, it is difficult to distinguish the difference in surface morphologies between these two membranes.

Atomic force microscopy (AFM) was used to examine the surface roughness of the prepared YSZ membranes. The scanned area was $2\ \mu\text{m} \times 2\ \mu\text{m}$, and AFM images of the outer surfaces of the prepared YSZ membranes are shown in Figure 4.5.



(a)



(b)

Figure 4.5 AFM images of YSZ membranes (1300 °C, 3 h) (a) original fibre and (b) after grafting

It can be seen that the surface of the grafted membrane is smoother than that of the nongrafted YSZ membrane. Table 4.2 also shows that the surface roughness of the grafted membrane decreased. After grafting, the mean roughness and root roughness decreased from 41 to 27.6 nm and from 53.4 to 33.6 nm, respectively. The smoother surface likely resulted from the grafted silane. This observation agrees well with the study of Yoshida et al., [44] who also found that the membrane surface roughness decreased after a grafting procedure was applied. It should be noticed that the thickness of grafted FAS on the membrane surface cannot be precisely measured by using AFM as this method is usually used to study on a very small surface area.

4.3.3 Membrane permeation characteristics

A bubble point test was carried out in characterizing prepared YSZ membranes. This method has been widely used in determining the maximum pore size ($>0.05\ \mu\text{m}$) present in a membrane, as well as the pore size distribution. [1, 36, 45-47] The bubble-point equation is

$$r_p = \frac{2\sigma}{p} \cos \theta$$

where r_p is the pore radius (m), σ is the surface tension at the liquid/air interface (N m^{-1}), p is the applied pressure (Pa), and θ is the contact angle (deg). The bubble-point test relies on the wetting of the membrane pore space by a wetting liquid. The minimum pressure required to force the liquid out of the pores is referred to as the bubble point, which is used to determine the maximum pore radius. [45, 46] The pore size distribution can be determined by a standard ASTM method. [36]

Figure 4.6 shows the pore size distributions (PSDs) of nongrafted and grafted YSZ hollow-fibre membranes. Q (%) is the percentage of the filter flow passing through active pores within a specified range. [36]

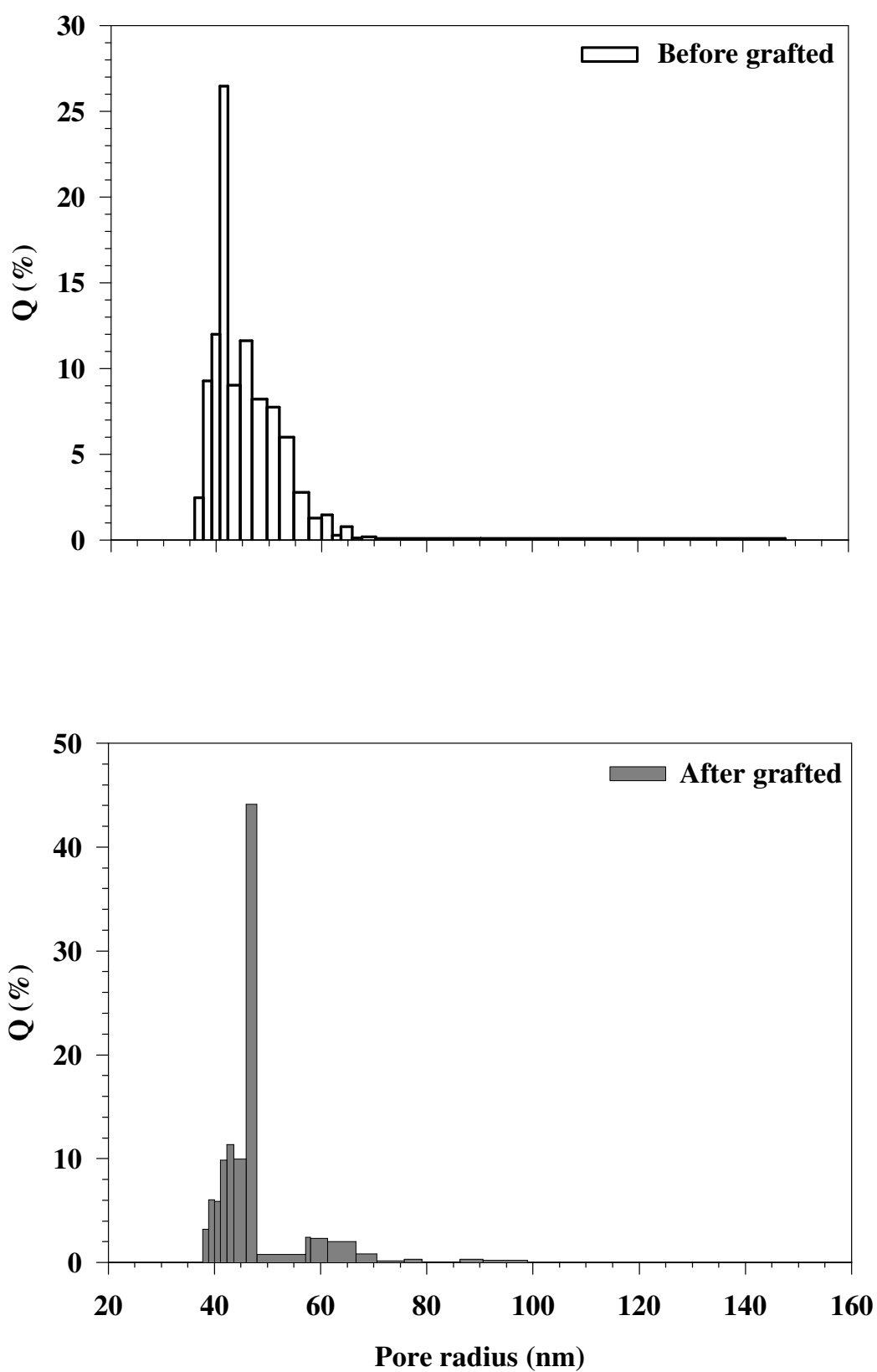


Figure 4.6 Membrane pore size distributions of prepared YSZ ceramic hollow-fibre membranes (1300 °C, 3 h)

It can be observed that the peak in the PSD for a nongrafted membrane is about 42 nm, whereas the peak in the PSD for a grafted membrane is about 48 nm.

The mean pore radius of the grafted YSZ membrane was slightly larger than that of the nongrafted variety. This is because the grafted FAS molecules can cover and seal very small pores, but the amount of FAS molecules might not be enough to cover and seal the large pores. The pore size of large pores remains. Thus, the mean pore radius of the grafted membrane was slightly increased. It also can be seen in Table 4.2 that the maximum pore size of the grafted YSZ hollow-fibre membrane was slight smaller than that of the original YSZ hollow-fibre membrane, indicating that FAS molecules might cover pores on the YSZ membranes.

4.3.4 Mechanical strength

The effect of sintering temperature on the mechanical strength of YSZ hollow-fibre membranes is shown in Figure 4.7, where the data were measured by a three-point bending test.

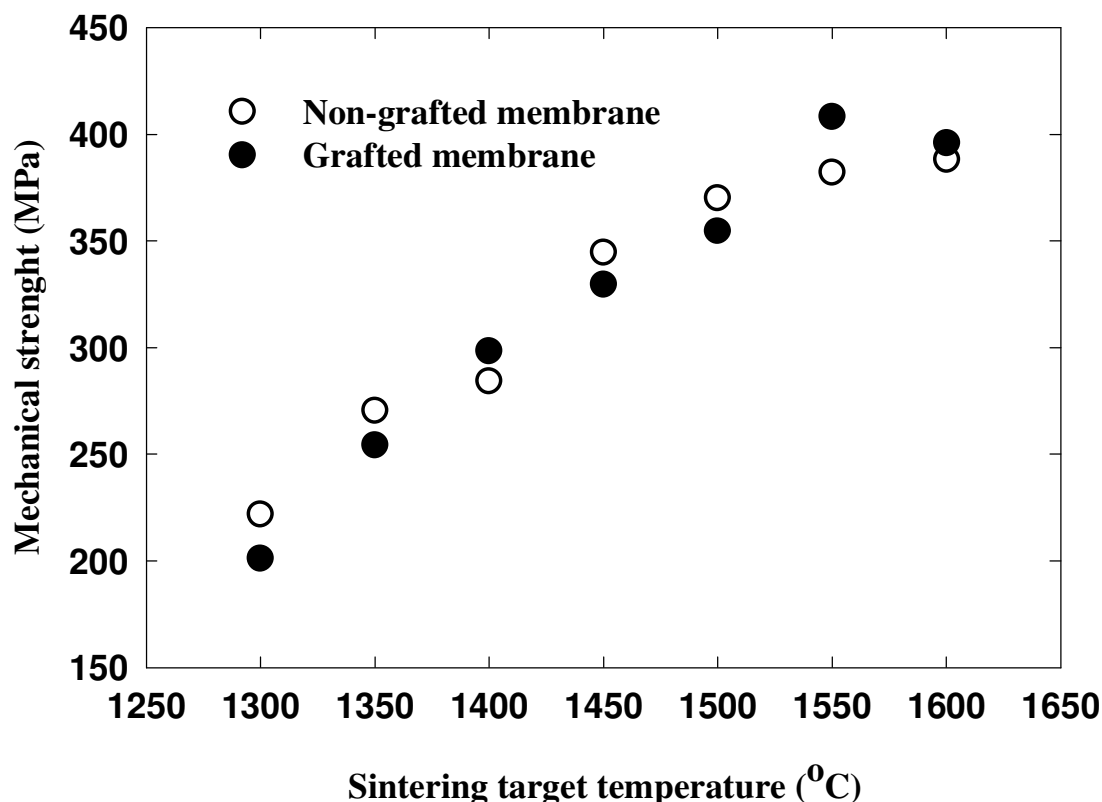


Figure 4.7 Mechanical strength of YSZ hollow-fibre membranes

As can be seen, the mechanical strength of the nongrafted YSZ hollow-fibre membranes sharply increased from 211 to 370 MPa as the sintering temperature was increased from 1300 to 1500 °C. It is believed that the porosity of the ceramic membrane decreases, resulting in a higher mechanical strength, when the sintering temperature is increased. However, as the sintering temperature was increased from 1500 to 1600 °C, the mechanical strength increased slowly from 370 to 388 MPa. This is believed to be the result of larger grain growth at higher sintering temperature. This trend of mechanical strength corresponds with the results of Liu et al., [48] indicating that the mechanical strength has an optimum value at a certain sintering temperature.

Figure 4.7 also shows that the differences in the mechanical strength between grafted and nongrafted YSZ membranes are very small. This indicates that the alkaline pretreatment and the small amounts of FASs (<1% of the membrane weight) do not influence the mechanical strength of the YSZ membrane. The previous literature shows that the mechanical strength of Al₂O₃ hollow-fibre membranes prepared with similar particle sizes and sintering conditions were in the range of 20-250 MPa, [49] which is lower than the values for the YSZ hollow-fibre membranes prepared in this work. This high mechanical strength of YSZ hollow-fibre membrane is beneficial for use of the membranes in practical applications.

4.3.5 Thermal and chemical stabilities

The thermal stabilities of grafted and nongrafted YSZ hollow-fibre membranes were examined using thermogravimetric analysis (TGA). A typical weight loss curve of a grafted membrane is shown in Figure 4.8.

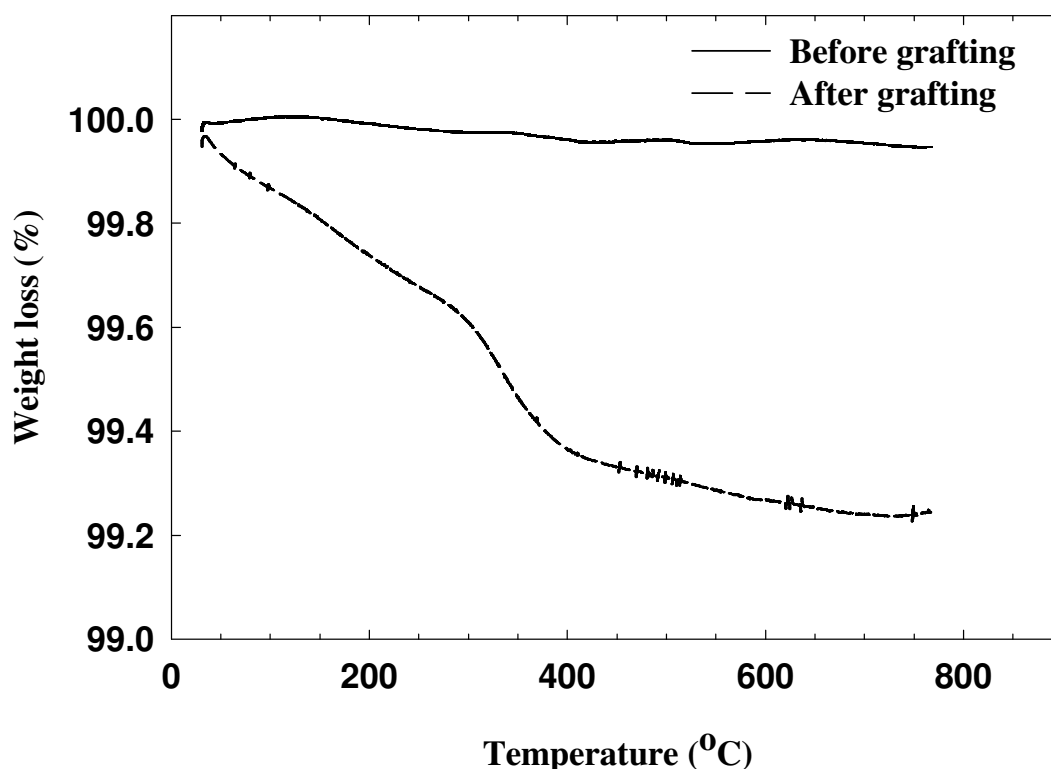


Figure 4.8 Percentage weight loss of nongrafted and grafted YSZ hollow-fibre membranes [alkaline pretreatment (pH 11) and grafting time = 8 h]

As can be seen, the weight loss from 100 to 270 °C was caused by physically adsorbed water and strongly hydrogen bonded water. [50] The steepest weight loss was observed at around 270 °C, where the silane component started to decompose. This result is consistent with the previous work by Koonaphapdeelert and Li [11] and Larbot et al., [40] who found grafted membranes to be thermally stable up to about 250 °C. Hexane was used as a testing solution for chemical stability, as it was also used as the grafting solvent. Table 4.3 shows the contact angles of YSZ hollow-fibre membranes sintered at 1300 °C under original conditions, under grafted conditions, and after being in contact with hexane for 100 h.

Table 4.3 Contact angles of YSZ membranes after contact with hexane for 100 h

Sintering temperature (°)	Grafting time (hour)	Contact angle (degree)		
		Original	Grafted fibre (with alkaline pre-treatment pH=11 for 8 hours)	After immersed in hexane for 100 hours
1300	8	64.55	134.35	133.24

The average dynamic contact angle of the membrane after in being contact with a cross-flow of hexane was slightly lower than that of the grafted membrane. However, the membrane maintained its hydrophobicity. No membrane swelling, cracking, or breaking was observed. This is clear evidence that FAS molecules were covalently bonded to the YSZ membrane and were stable in hexane.

4.4 Conclusions

A robust and hydrophobic YSZ hollow-fibre membrane was successfully developed in this study. After an alkaline pretreatment, the grafted YSZ hollow-fibre membranes showed a dynamic contact angle of up to 140°. The overall morphologies of the membranes were maintained after the FAS grafting process, and they showed high mechanical strength, which is important for practical applications. The grafted membranes also showed thermal stability up to 270 °C and chemical stability in hexane.

These results provided some information on how to efficiently restore the hydroxyl groups on the ceramic membrane surface and further enhance the grafting process.

The grafted YSZ hollow-fibre membranes exhibited high hydrophobicities, high mechanical strengths, and considerable thermal and chemical stabilities. The membranes prepared in this study have great potential in applications for solvent separation or as membrane contactors for aqueous media.

4.5 References

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Chapter 5 Carbon dioxide absorption in aqueous monoethanolamine solutions using hydrophobic ceramic hollow-fibre membranes

Abstract

Membrane contactors packed with hydrophobic ceramic hollow-fibre membranes have been applied to carbon dioxide absorption by aqueous monoethanolamine solution. The problems such as flooding, foaming and loading which exist in packed columns were not observed in this study. After absorption experiments, the ceramic hollow-fibre membranes retained their hydrophobicity and mechanical stability which is not the case for polymeric hollow-fibre membranes. The height of transfer unit (HTU) of the membrane contactor was in the range of 0.16 to 0.38m at 293K and was around 1.4m at 333K. Compared to conventional packed columns and polymeric hollow-fibre membranes, the values of the HTU are relatively small, indicating its outstanding absorption efficiency over a wide temperature range. The theoretically predicted mass transfer coefficients were in good agreement with the experimental results.

5.1 Introduction

One of the largest environmental issues which humans are facing is global warming which is mainly caused by greenhouse gases such as carbon dioxide, methane, chlorofluorocarbons and nitrogen oxide in the atmosphere. Among them, CO₂ is the largest contributor to greenhouse gases and is responsible for more than 50 percent of global warming effects. [1]

About 40 percent of CO₂ emissions are from the combustion of fossil fuels (coal, natural gas, heavy hydrocarbons) as they are used to supply energy for more than 85% of power generation in the world. [2] It has become very important to reduce CO₂ emissions from the combustion of fossil fuels. There are several options to reduce CO₂ emissions, such as a reduction in energy requirement, efficient usage of energy (fuel cell), alternative energy (hydrogen, renewable energy) and CO₂ capture. Among them, CO₂ capture is being considered as a transitional solution to mitigate the

environmental impact until the development of renewable energy technologies reached its maturity. [3]

Several techniques such as absorption/stripping, membrane separation, chemical reaction cycles and decarbonation of fuels before combustion have been used for CO₂ capture. Chemical absorption/stripping using Monoethanolamine (MEA) solution is a proven commercialized process for CO₂ capture. In the process, MEA solution is in contact with flue gas in an absorber such as a packed column where CO₂ is removed by the solution. The overall reaction is shown below: [4]



MEA reacts with CO₂ in an absorber to form MEA carbamate. The CO₂-rich MEA solution is then delivered to a stripper where it is heated to release pure CO₂ and MEA. The released CO₂ can be used for carbonation of beverages, dry ice production or stored in a compressed form in geological reservoirs. The retained MEA solution is recycled to the absorber. However, a packed column is not economical as it requires considerable space. As demonstrated by Idem et al., the length of a CO₂ absorption packed column is about 10 meters with a diameter of about 0.3 meters. [5] In addition, a limitation of a pack column is that CO₂ can only be removed from the regions where gas and liquid are properly in contact. Proper control of gas and liquid flow rates must be carried out in order to prevent flooding, foaming, channelling and entrainment problems which increase the operating and maintenance costs.

Currently, hollow-fibre membrane contactors have been proven to have several advantages compared with packed columns. First, the larger surface area/volume ratio of a hollow-fibre membrane module is more economical to use compared to a packed column. According to studies by Falk-Pedersen et al., membrane contactors are smaller and lighter than packed columns by 72% and 66%, respectively. [6] Second, gas and liquid flow on different sides (i.e., shell and lumen sides) of a hollow-fibre membrane and thus can be operated independently without flooding, loading and channelling problems. Other advantages such as higher efficiency, simple scale up and a known gas-liquid interfacial area have been reported by Gabelman et al. and Li et al. [7, 8]

Most membranes in membrane contactors are made from polymeric materials such as polypropylene (PE), polysulphone (PS) and polydimethylsiloxane (silicon rubber) etc. However, polymeric membranes are not durable over long term operation as they can be wetted or corroded by absorbent, leading to poor performance during the absorption process. [6, 9-11]

Ceramic membranes are well known for their superior thermal and chemical stability and therefore provide an alternative for a membrane contactor. In a membrane contactor, the membrane acts as a medium to provide a contact area for gas and liquid. Membranes must be operated in a non-wetted configuration to prevent flooding and entrainment problems.

Luis et al. [12] demonstrated that a ceramic hollow-fibre membrane contactor can be used for sulphur dioxide absorption. In their study, hydrophilic Al_2O_3 ceramic hollow-fibre membranes were used in a membrane contactor and *n,n*-dimethylaniline was used as an absorbent. However, the absorbent, *N,N*-dimethylaniline, is an organic solvent which may dissolve or damage the sealing parts between membranes and the housing of membrane contactor during long term operation so it is believed that an aqueous absorbent is a better option for long term operation. However, most ceramic membranes are limited use in membrane contactors due to their hydrophilic nature. Several studies have focused on the fabrication of hydrophobic ceramic hollow-fibre membranes prepared by surface modification methods. [13] Koonaphapdeelert et al reported that a hydrophobic ceramic hollow-fibre membrane was successfully used for CO_2 stripping from a aqueous absorbent. [14]

In this study, a YSZ based hydrophobic ceramic membrane contactor is used for CO_2 absorption from an aqueous absorbent. The module performance, effects of operation conditions and mass transfer model were studied in order to thoroughly understand the CO_2 absorption process using a hydrophobic ceramic membrane contactor.

5.2 Experimental

5.2.1 Chemicals

8 mol% yttria stabilized zirconia (YSZ) powders with particle sizes of 0.25 μm ($d_{50}=0.25 \mu\text{m}$, surface area 8-13 $\text{m}^2 \text{g}^{-1}$) and 10nm ($d_{50}=10\text{nm}$, surface area 154 $\text{m}^2 \text{g}^{-1}$) and purchased from NexTech Materials Ltd. (Ohio) were used for the preparation of YSZ ceramic hollow-fibre membranes. Polyethersulfone (PESf, Radel A300, Ameco Performance, USA), 1-methyl-2-pyrrolidinone (NMP, HPLC grade, Sigma-Aldrich) and Solsperse 3000 (Noveon Inc., Ohio) were used as the binder, the solvent and the additive, respectively. Fluoroalkylsilanes (FAS, Lancater Synthesis) and hexane (HPLC grade, Sigma-Aldrich) were used for the surface grafting process. Monoethanolamine (MEA) was supplied from Univer plc. A 14% CO_2 and 86% N_2 gas mixture was purchased from BOC (UK).

5.2.2 Membranes and modules

YSZ hollow-fibre membranes sintered at a temperature of 1300 $^{\circ}\text{C}$ were used in this study. An improved surface modification technology was carried out in this study in order to increase the hydrophobicities of YSZ fibres. The improved technology involved alkaline pre-treatment and a common surface modification technology. For alkaline pre-treatment, the sintered YSZ hollow-fibre membranes of 30 cm in length were sealed off at both ends and then immersed into an alkaline solution ($\text{pH}=11$) for 8 hours. The pre-treated fibres were then dried in an oven at 100 $^{\circ}\text{C}$ for 24 hours. After cooling, the pre-treated fibres were ready for surface modification. The surface modification procedure involves the following steps: (i) rinsing pre-treated YSZ fibres with hexane in an ultrasonic bath, (ii) drying in air, (iii) grafting of FAS on the membrane surface at 40 $^{\circ}\text{C}$ in a solution containing 0.02M FAS in hexane for 10 hours, (iv) removal of YSZ fibres from the grafting solution, (v) rinsing of grafted YSZ fibres with hexane in an ultrasonic bath, (vi) drying at 100 $^{\circ}\text{C}$ for 24 hours. After cooling, the grafted fibres were ready for the preparation of membrane module. A module was made using two male-run-tee connectors and a one half inch stainless steel tube. The assembled module was packed with the desired number of fibres. At

both ends of the module, the open area between the fibres was sealed off using epoxy resin (UK epoxyresins). The module configurations are shown in Table 5.1.

Table 5.1 The configuration of hydrophobic YSZ membrane module

	Module 1	Module 2
Fibre properties		
I.D. (mm)	0.64	0.64
O.D. (mm)	0.85	0.85
Mean pore radius (um) (based on gas permeation measurement)	0.46	0.46
Effective porosity (m^{-1}) (based on gas permeation measurement)	1527	1527
Module properties		
Diameter (mm)	10.1	10.1
Effective length (mm)	130	140
Number of fibres	21	24
Volume ($m^3 \times 10^5$)	1.04	1.12
Membrane contact area ($m^2 \times 10^3$)	7.29	8.97
Surface area per volume ($m^2 m^{-3}$)	700	800

5.2.3 Absorption setup

The experimental configuration is shown in Figure 5.1.

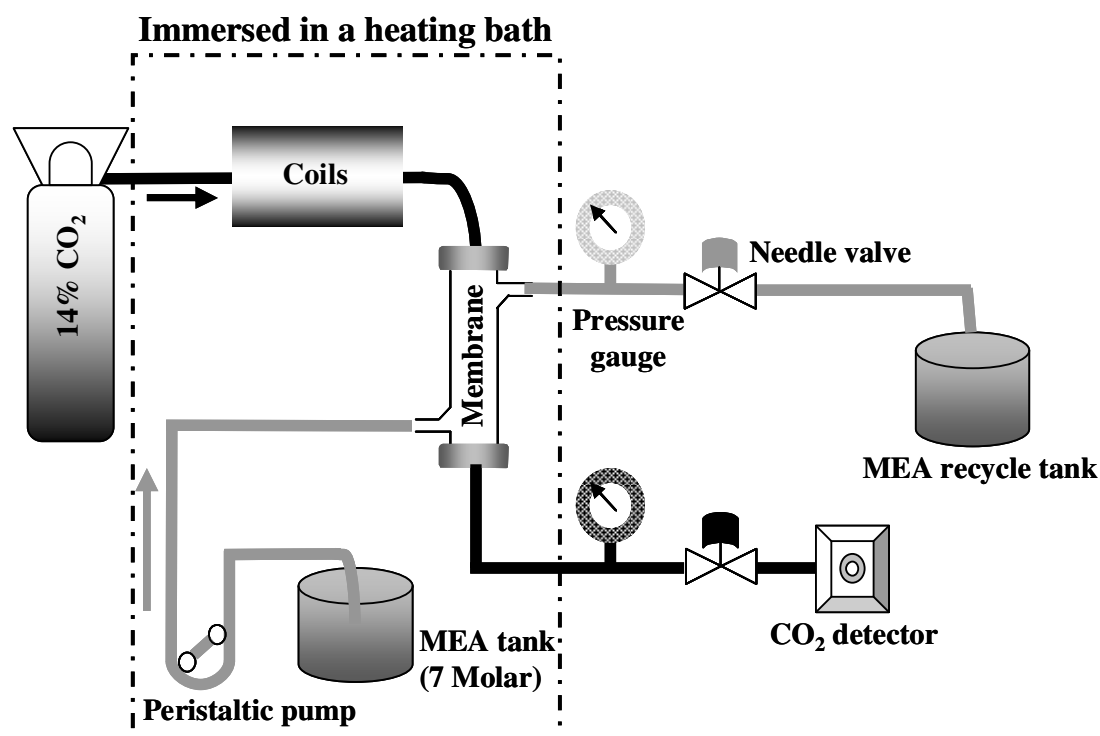


Figure 5.1 The experimental configuration of CO₂ absorption in a hydrophobic YSZ hollow-fibre membrane module.

The absorption column was packed with hydrophobic YSZ hollow-fibre membranes and placed in a heating bath (Grant GD120). The CO₂ flow rate was controlled by a gas flow control system (Brooks Instrument 0152) and fed to the membrane module from the lumen side. A CO₂ detector (Servomex 1440) was used to monitor the volume percentage of CO₂ from the outlet of the module. MEA was fed into the module from the shell side using a peristaltic pump (Watson Marlow 505U). The gas and liquid flows were operated in counter-current mode. In the membrane contactor, the pressure difference of the gas and liquid phases was maintained between 10 kPa and 15 kPa by needle valves to achieve a stable gas-liquid interface. Different MEA and CO₂ flow rates at various temperatures were examined in this study.

5.3 Theory

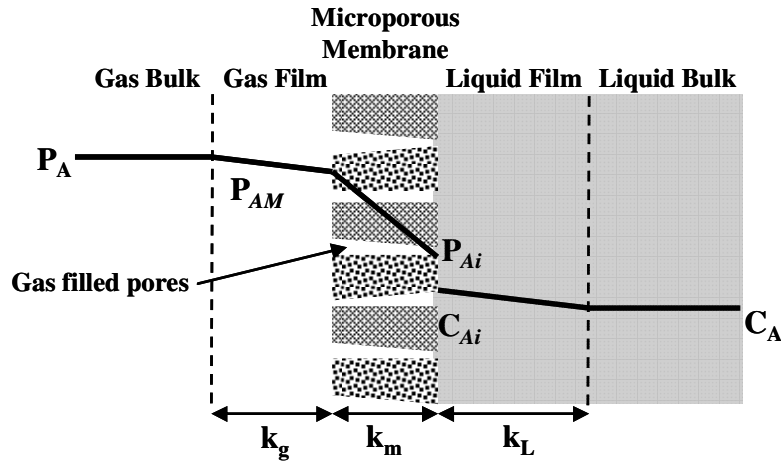


Figure 5.2 Mass transfer model of an ideal gas-filled pores membrane

In the study, the membrane contactor was operated in a non-wetted mode as packed YSZ membranes were hydrophobic. The membrane pores in the hydrophobic membrane are assumed to be filled with gas. As shown in Figure 5.2, an liquid solution which does not wet the membrane flows on one side of the membrane, while a gas mixture containing gas A flows on the other side of the membrane at a pressure less than that liquid phase.

Mass transfer occurs in three different phases: the gas film, the membrane and the liquid film. Local rate of the gas A transfer, N_A through the membrane at steady state can, therefore described as:

$$N_A = k_{Ag} (P_A - P_{AM}) A_M \quad (5.1)$$

$$= k_{AM,g} (P_{AM} - P_{Ai}) A_M \quad (5.2)$$

$$= k_{AL} (C_{Ai} - C_A) A_M \quad (5.3)$$

$$= K_{Ag} (P_A - P_{A,e}) A_M \quad (5.4)$$

$$= K_{AL} (C_{A,e} - C_A) A_M \quad (5.5)$$

where k_{Ag} , $k_{AM,g}$ and k_{AL} are the individual mass transfer coefficients in gas film, membrane and liquid film, respectively. A_M is the mass transfer total area calculated from d_i , d_o or d_m , depends on the region of mass transfer, which are the liquid film, the membrane and the gas film, respectively. The P_{Ai} and C_{Ai} are the partial pressure

and concentration of A at interface, respectively. $P_{A,e}$ and $C_{A,e}$ are the equilibrium partial pressure and concentration of A in gas and liquid phase, respectively and they may be related by Henry's law:

$$P_{Ai} = H_A C_{Ai} \quad (5.6)$$

$$P_{A,e} = H_A C_A \quad (5.7)$$

$$P_A = H_A C_{A,e} \quad (5.8)$$

where H_A is a Henry's law constant of component A. Therefore, the overall mass transfer coefficient, K_{Ag} through a non-wetted hydrophobic membrane can be predicted by a resistance in series model as follow: [8, 15]

$$\frac{1}{K_{Ag}} = \frac{d_i}{k_{Ag} d_o} + \frac{1}{k_{AM,g}} + \frac{H_A}{k_{AL}} \quad (5.9)$$

In this case, the liquid phase contains chemicals which can react with the gaseous solute and further increase the mass transfer rate. The effect of chemical reaction on the mass transfer is expressed in the form of the enhancement factor (E). The enhancement factor is defined as the ration of the chemical mass transfer flux over the physical mass transfer flux as expressed in Eq. (5.10)

$$E = \frac{J_{chem}}{J_{phy}} \quad (5.10)$$

where J_{chem} and J_{phy} are the absorption fluxes due to chemical reaction and due to physical absorption respectively. The term E is incorporated into the local rate of mass transfer in the liquid. Eq (5.3) can be rewritten as:

$$N_A = Ek_L (C_{Ai} - C_A) A_M \quad (5.11)$$

Thus the overall mass transfer coefficient can be rewritten as

$$\frac{1}{K_{Ag}} = \frac{d_i}{k_{Ag} d_o} + \frac{1}{k_{AM,g}} + \frac{H_A}{Ek_{AL}} \quad (5.12)$$

The calculations of individual mass transfer coefficients, enhancement factor and Henry's number are described in following sections.

5.3.1 Mass transfer coefficient of gas phase

The mass transfer coefficient in the gas phase can be determined by Eq. (5.13)

$$k_g = Sh \frac{D_{g,b}}{d_i} \quad (5.13)$$

where $D_{g,b}$ is the bulk CO₂ diffusion coefficient in the gas phase (m² s⁻¹) and Sh is the Sherwood number.

The bulk CO₂ diffusivity in the gas phase can be determined by the following equation: [16]

$$D_{g,b} = \frac{1.8583 \times 10^{-7} \times T^{3/2}}{P \sigma_{g,b}^2 \Omega_{Dg,b}} \times \sqrt{\frac{1}{M_g} + \frac{1}{M_b}} \quad (5.14)$$

where M_g is the molecular weight of CO₂; M_b is the molecular weight of N₂, P is pressure (atm), T is temperature (K), $\sigma_{g,b}$ is the Lennard-Jones parameter (Å) and $\Omega_{Dg,b}$ is the diffusion collision integral (dimensionless). $\sigma_{g,b}$ and $\Omega_{Dg,b}$ can be obtained from Perry's Chemical Engineerings' Handbook.

The Sherwood number can be expressed by as an engineering correlation by Eq. (5.15). [17]

$$Sh = 1.64 \cdot Pe^{0.33} \quad (5.15)$$

where Pe is the Peclet number. Pe can be obtained from Eq. (5.16).

$$Pe = \frac{d_e^2 \cdot \mu_g}{D_{g,b} \cdot \ell \cdot \rho_g} \quad (5.16)$$

where d_e , ℓ , are the hydraulic diameter and the length of the hollow-fibre membrane (m); μ_g , $D_{g,b}$, ρ_g are the viscosity (Pa s), diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) and density (kg m^{-3}) of the gas, respectively. The viscosity of a mixture of gases can be obtained from Perry's Chemical Engineerings' Handbook.

5.3.2 Mass transfer coefficient of membrane

The mass transfer coefficient in the membrane can be written as Eq. (5.17) [4]

$$k_m = \frac{D_{g,p} \epsilon_p}{L_p} \quad (5.17)$$

where $D_{g,p}$ is the effective CO_2 diffusion coefficient in the membrane pores ($\text{m}^2 \text{s}^{-1}$), ϵ_p and L_p are the effective porosity (dimensionless) and the effective pore length (m) of the hollow-fibre membrane, respectively.

The effective CO_2 diffusion coefficient in gas filled pores can be expressed by the combined processes of bulk diffusion and Knudsen diffusion. [18]

$$\frac{1}{D_{g,p}} = \frac{1}{D_{g,b}} + \frac{1}{D_k} \quad (5.18)$$

where D_k is the Knudsen diffusion coefficient of CO_2 ($\text{m}^2 \text{s}^{-1}$) which is given by Eq. (5.19):

$$D_k = \frac{1}{3} d_p \sqrt{\frac{8RT}{\pi M}} \quad (5.19)$$

where d_p is the mean pore diameter (m); M is the molecular weight of the gas (kg kmol^{-1}); R is the gas constant ($\text{J kmol}^{-1} \text{K}^{-1}$) and T is the temperature (K).

5.3.3 Mass transfer coefficient of liquid phase

The mass transfer coefficient in the liquid phase is described by Eq. (5.20) [17]

$$k_L = \frac{Sh \cdot D_{g,L}}{d_o} \quad (5.20)$$

where $D_{g,L}$ is the diffusion coefficient of CO_2 in the liquid phase (MEA) ($m^2 s^{-1}$). $D_{g,L}$ cannot be determined directly due to the chemical reaction resulting from CO_2 absorption in liquid phase. Nitrous oxide (N_2O) which has a similar configuration, molecular volume and electronic structure as CO_2 has been employed as a non-reacting gas to estimate the diffusivity of CO_2 . Sada et al. [19] have developed a correlation between N_2O diffusivity and CO_2 diffusivity. The diffusivity data for N_2O can be obtained from the literature as reported by Versteeg et al. [20] The reported correlation can be used to determine the diffusivity of CO_2 in MEA solution at different temperatures.

The Sherwood number for the hollow-fibre contactor can be expressed as an engineering correlation by Eq. (5.21): [17, 18]

$$Sh = 0.32 \cdot Re^{0.61} \cdot Sc^{0.33} \quad (5.21)$$

where Re is the Reynolds number and Sc is the Schmidt number. The Re and Sc number are given by Eq. (5.22) and (5.23).

$$Re = \frac{\rho_L \cdot v_L \cdot d_e}{\mu_L} \quad (5.22)$$

$$Sc = \frac{\mu_L}{\rho_L \cdot D_{g,L}} \quad (5.23)$$

where ρ_L , v_L , μ_L are the density ($kg m^{-3}$), superficial velocity ($m s^{-1}$) and viscosity (Pa s) of the liquid, respectively. The density and viscosity of MEA solution at different temperatures can be estimated by the correlations reported by Maceiras et al. [21]

5.3.4 The Henry's law constant

The Henry's law constant can be determined from Eq. (5.24): [22]

$$H_A(T) = H_A(T_0) \times \text{Exp}\left[-C\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (5.24)$$

where $H_A(T_0)$ is the Henry's law constant of CO_2 at a reference temperature (298K), this value was found to be equal to 0.034 (atm L mole^{-1}); Constant C is equal to 2400 (K) for CO_2 gas. The Henry's constants above are in the unit of atm L mol^{-1} which can be converted into a dimensionless form by multiplying with 24.46 ($\text{mole L}^{-1} \text{atm}^{-1}$). [23]

5.3.5 Enhancement factor

The enhancement factor (E) relies on reaction kinetics and reaction components. Westerterp et al. and Feron et al. have developed a mathematical equation to estimate the enhancement factor for a CO_2 -MEA system in a hollow-fibre membrane contactor. [18, 24] Since the absorption reaction at the gas/liquid contact interface is assumed to be instantaneous, the enhancement factor can be described by Eq. (5.25).

$$E = \left(1 + \frac{D_{\text{MEA,water}} C_{\text{MEA}}}{n D_{\text{CO}_2,\text{MEA}} C_{\text{CO}_2,i}}\right) \times \left(\frac{D_{\text{CO}_2,\text{MEA}}}{D_{\text{MEA,water}}}\right)^{\frac{1}{3}} \quad (5.25)$$

where C_{MEA} is the bulk concentration of MEA (mol m^{-3}); $D_{\text{MEA,water}}$ is the diffusivity of MEA in water ($\text{m}^2 \text{s}^{-1}$); $D_{\text{CO}_2,\text{MEA}}$ is the diffusivity of CO_2 in MEA solution ($\text{m}^2 \text{s}^{-1}$); $C_{\text{CO}_2,i}$ is the CO_2 concentration at the gas/liquid interface (mol m^{-3}) and n is the reaction stoichiometry. According to the two films theory, the amount of solute diffusing from the gas phase to the interface must equal the amount of solute diffusing from the interface to the liquid phase. [25] Therefore, the absorption rate of CO_2 from the gas phase and to the liquid phase can be assumed to be identical, and hence, the following relation holds: [26]

$$R_{\text{CO}_2} = k_g (P_{\text{CO}_2} - P_{\text{CO}_2,i}) = E \cdot k_L (C_{\text{CO}_2,i} - C_{\text{CO}_2,L}) \quad (5.26)$$

where R_{CO_2} is the absorption rate of CO_2 ($\text{mol m}^{-2} \text{ s}^{-1}$); P_{CO_2} is the partial pressure of CO_2 in the bulk gas phase (kPa); $P_{\text{CO}_2,i}$ is the partial pressure of CO_2 at the gas-liquid interface (kPa); $C_{\text{CO}_2,i}$ is the concentration of CO_2 at the gas-liquid interface (mol m^{-3}); $C_{\text{CO}_2,L}$ is the concentration in the liquid phase (mol m^{-3}).

$C_{\text{CO}_2,L}$ can be considered to be zero as the reaction is assumed to be instantaneous. By applying Henry's law, Eqn. (5.26) can be rewritten as:

$$k_g \cdot H(C_{\text{CO}_2} - C_{\text{CO}_2,i}) = E \cdot k_L \cdot C_{\text{CO}_2,i} \quad (5.27)$$

$C_{\text{CO}_2,i}$ can be evaluated by rearranging Eq. (5.25) and (5.27) and used for the calculation of enhancement factor.

5.3.6 Experimental overall mass transfer coefficient

For the non-wetted membrane, the experimental overall mass transfer coefficient can be more convenient expressed using Eq. (5.28) [27]

$$K_g = \frac{Q_g}{A} \ln\left(\frac{C_{\text{CO}_2,\text{in}}}{C_{\text{CO}_2,\text{out}}}\right) \quad (5.28)$$

where K_g is the overall mass transfer coefficient for CO_2 (m s^{-1}); A is the gas-liquid interfacial area (m^2); Q_g is the gas flow rate ($\text{m}^3 \text{ s}^{-1}$); $C_{\text{CO}_2,\text{in}}$ and $C_{\text{CO}_2,\text{out}}$ are the CO_2 concentrations in the gas phase at the inlet and outlet, respectively.

5.3.7 The height of transfer unit (HTU)

The efficiency and performance of packed columns and membrane contactors are often presented by using the height of transfer unit (HTU). [14, 28] A small HTU indicates that a shorter length of column is required for separation i.e. it is more efficient and economical. HTU can be obtained from the differential mass balance equation in the gas phase. The differential mass transfer balance in the gas phase is illustrated in Eq. (5.29)

$$V \frac{dy}{dz} = K_G n' \pi d_i (y^* - y) \quad (5.29)$$

where V is the molar gas flow rate (mol s^{-1}); y is the mole fraction of CO_2 in the gas phase (dimensionless); z is the length measured from the bottom of the column; n' is the number of fibres; d_i is the inner diameter of fibre (m); and y^* is the equilibrium mole fraction of gas. Integrating Eq. (5.29) from the bottom of the column gives,

$$\ell = \frac{V}{K_G n' \pi d_i} \int_{y_0}^{y_t} \frac{dy}{y^* - y} \quad (5.30)$$

where ℓ is the length of the hollow-fibre membrane (m); y_t and y_0 are the gas mole fractions at the top and bottom of the column, respectively. Eq. (5.30) can be rewritten as:

$$\ell = \text{HTU} \times \text{NTU} \quad (5.31)$$

where HTU and NTU are the height and number of transfer units, respectively which can be described by Eq. (5.32) and (5.33).

$$\text{HTU} = \frac{V}{K_G n' \pi d_i} = \frac{v_g}{K_G \cdot a} \quad (5.32)$$

and

$$\text{NTU} = \int_{y_0}^{y_t} \frac{dy}{y^* - y} \quad (5.33)$$

where v_g is the superficial gas velocity (m s^{-1}) and a is the gas-liquid interfacial area per unit volume ($\text{m}^2 \text{ m}^{-3}$).

5.4 Results and discussion

5.4.1 Module performance

The membrane performance can be presented as HTU which was calculated by using Eq. (5.32). The HTU values for Module 1 under different operating conditions are shown in Figure 5.3.

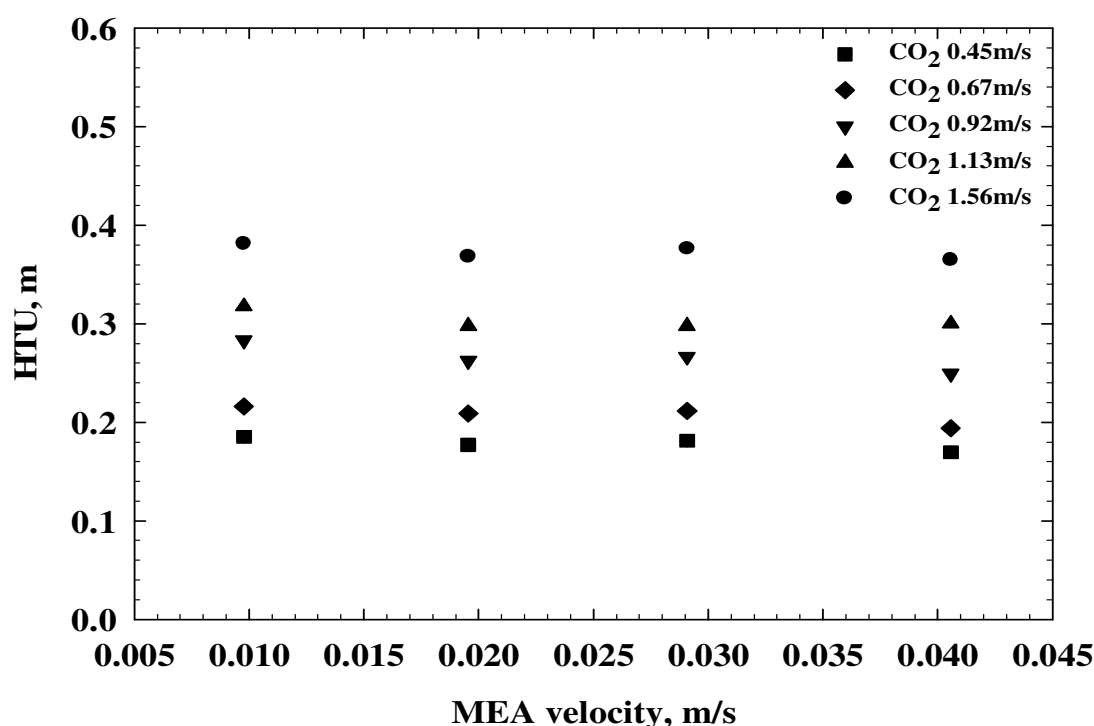


Figure 5.3 Effect of liquid flow rate on HTU with different CO₂ flow rate in Module 1 at 293K,

It can be seen that the HTU values remained constant as the liquid flow rate increased but increased with the increasing gas flow rate. The observations were expected as the HTU values are directly proportional to the gas velocity. It is observed that the HTU values are in the range between 0.16 and 0.38. Compared to the HTU of conventional packed columns which is in the range of 3.0 to 4.9, [28] the present membrane contactor showed a better performance. This can be attributed to two reasons. The first reason is its larger interfacial area per unit volume, which provides more contact area for gas-liquid absorption. The other reason is that the hydrophobic membrane prevents flooding and foaming during absorption. Gas could

be absorbed immediately as it contacted with the liquid phase. Therefore, the HTU of ceramic hollow-fibre contactors is smaller than that of a packed column.

5.4.2 Effect of temperature on membrane performance

Figure 5.4 shows the HTU of Module 1 operating at different temperatures. As can be seen, the HTU increased with the operating temperature at a constant gas velocity. The HTU was in the range from 3.96 to 4.09 when the operating temperature was raised to 333K.

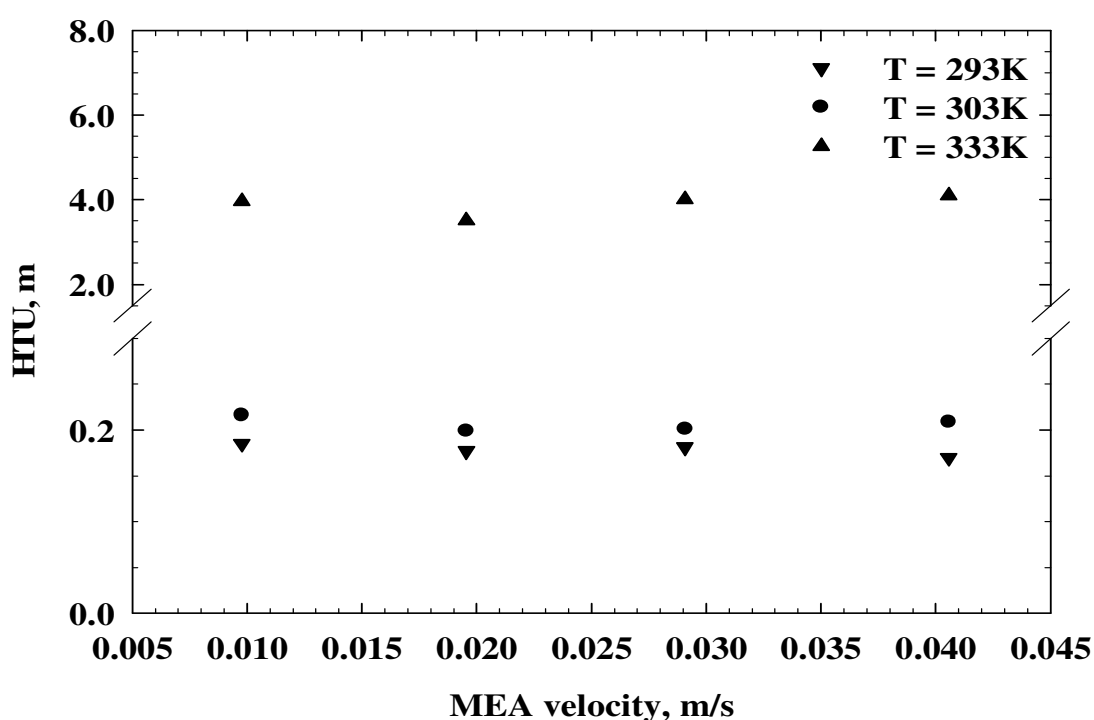


Figure 5.4 HTU of Module 1 at different temperature, CO₂ velocity 0.45 m s⁻¹

This larger HTU resulted from the poor solubility of CO₂ at high temperature, although the high operating temperature benefits the reaction kinetics. [21] Since the advantages of ceramic hollow-fibre membranes are their thermal and chemical stability at high operating temperature and their high surface area per volume ratio, the performance of ceramic hollow-fibre modules was further examined at high temperature with high absorbent concentration and at different surface area per volume ratios in following studies.

5.4.3 Effect of absorbent concentration on membrane performance

Figure 5.5 shows the HTU of Module 1 operating at different concentrations of liquid absorbent.

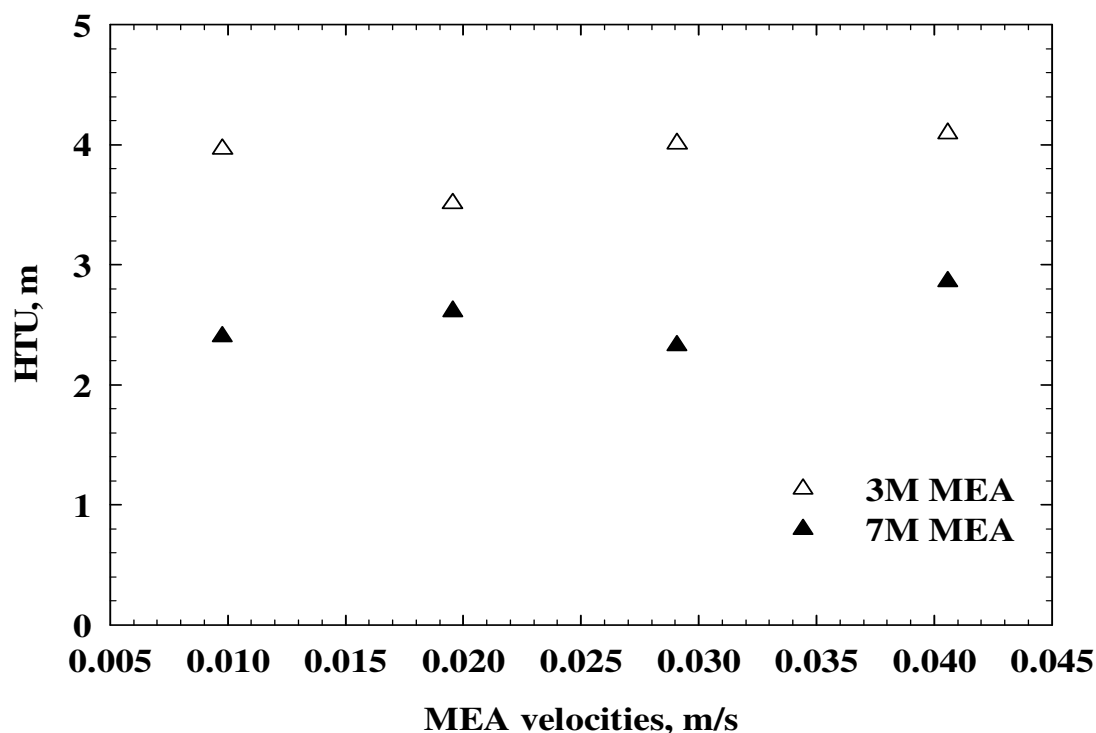


Figure 5.5 HTU of Module 1 with varied absorbent concentration at 333K, CO₂ velocity 0.45m s⁻¹

The HTU values were smaller at a 7M MEA absorbent concentration than at a 3M MEA concentration as the absorption capacity of the liquid solution was enlarged at a higher concentration, implying the performance of absorption has been improved at a 7M MEA solution. It should be noted that most polymeric hollow-fibre membranes are usually operated at a lower concentration (0.8-5M) of MEA and at a relatively lower operating temperature of around 40 °C to maintain their integrity. [29-31] Some polymeric membranes made from PE, PESf and silicon rubber were observed to be wetted by aqueous absorbent after a pilot absorption test. [6] In this study, however, there is no corrosion or wetting observed in the ceramic hollow-fibre membranes during the absorption experiments.

5.4.4 Effect of surface area per volume on membrane performance

To achieve better performance, ceramic hollow-fibre contactors with different surface area per volume ratios were studied and their performances are shown in Figure 5.6.

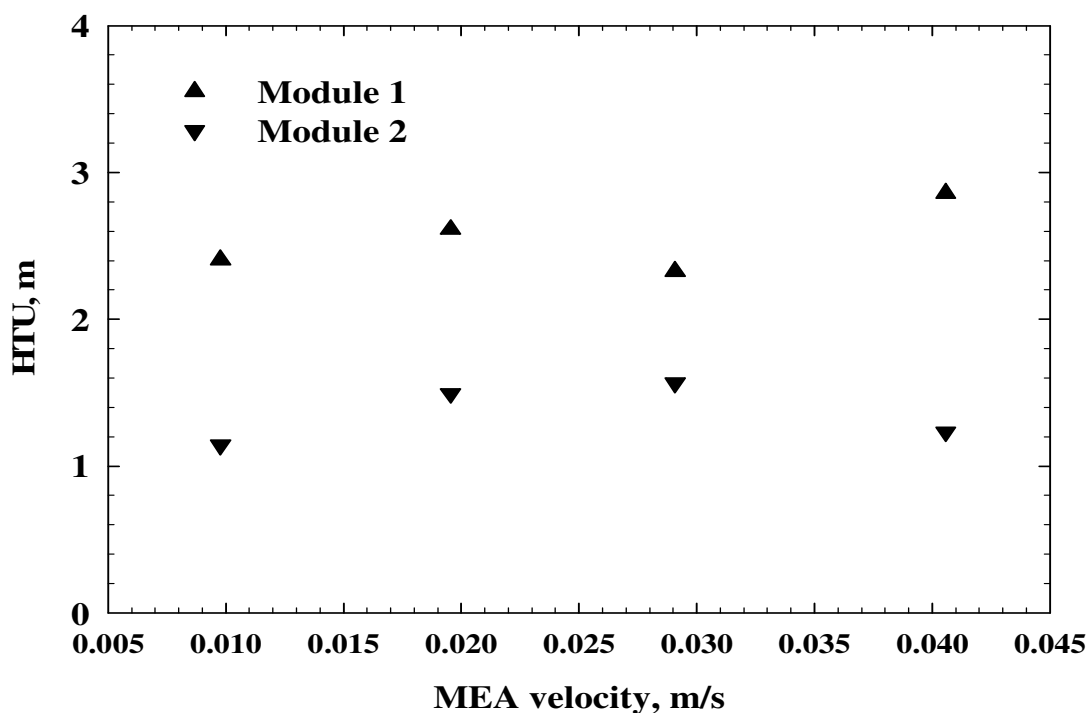


Figure 5.6 Effect of liquid flow rate on HTU with different module at 333K, 7M
MEA and CO₂ velocity 0.45m s⁻¹

Module 2 with a higher surface area per volume showed a lower HTU at a constant gas velocity. The HTU of Module 2 is about 1.4 which is relatively higher than the HTU of Module 1 at 293K (as shown in Fig. 5.3). The poor performance of the membrane module at high temperature could be caused by the reaction kinetics and solubility of the absorbent. Although MEA is a chemically stable and relatively cheap absorbent for CO₂ absorption, it could probably not be a good absorbent for high temperature absorption. However, the HTU of Module 2 is approximately one third of the HTU of packed columns which operated at room temperature. This performance still can compete with a conventional packed column. Nevertheless, it is believed the performance of ceramic membrane module can be improved as an ionic liquid is applied for the high temperature absorption. [32]

5.4.5 Effect of gas flow rate on overall mass transfer coefficient

The experimental overall mass transfer coefficient can be calculated from Eq. (5.28). It can be seen from Figure 5.7, that K_g is a function of gas velocity at different liquid velocities

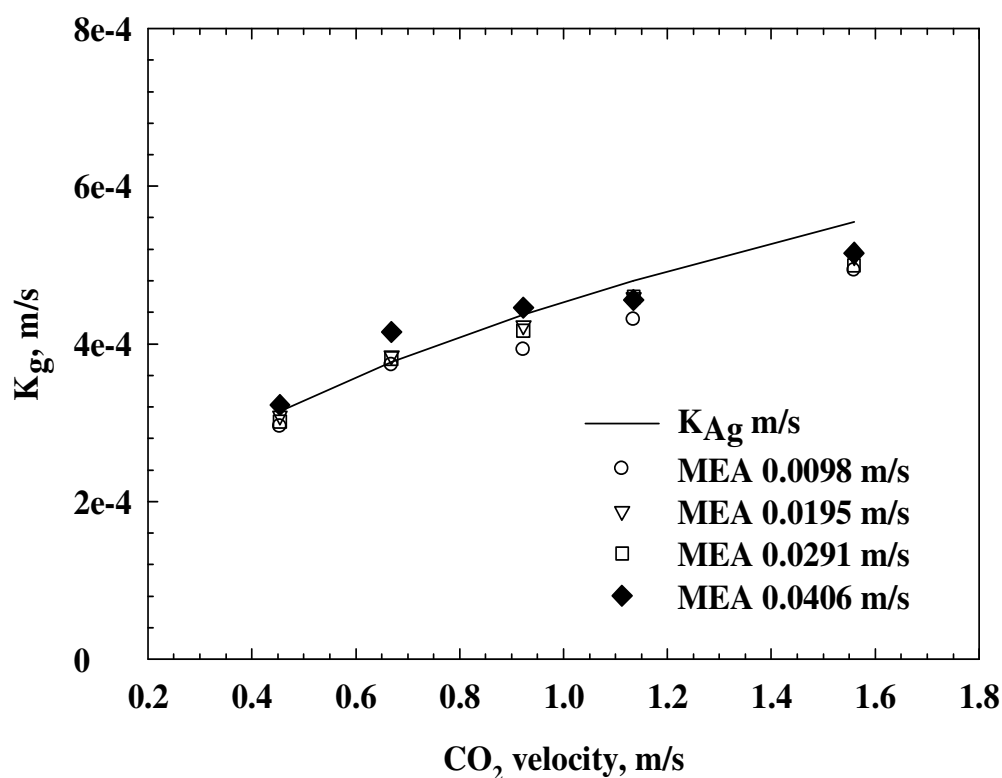


Figure 5.7 Effect of gas flow rate on overall mass transfer coefficient in Module 1 at 293K.

The overall mass transfer coefficient increased with the gas velocity since a high gas velocity could effectively reduce the mass transfer resistance in the gas phase and therefore improve the overall mass transfer. $K_{A,g}$ can also be theoretically calculated from Eq. (5.12). They are also shown as a solid line in Figure 5.7. The predicted mass transfer coefficient also followed a similar trend as experimental K_g values which increased when gas velocity increased. The experimental results agreed well with the theoretical prediction. In contrast, the liquid flow rate was found to have less influence on the overall mass transfer coefficient which is a well understood phenomenon.

5.4.6 Hydrophobicity of YSZ hollow-fibre membrane

The hydrophobicity of YSZ membranes is very important for gas/liquid absorption since they are used as a medium to prevent wetting problems in membrane modules. The hydrophobicity can be measured by contact angle measurements and it has been suggested that a contact angle of 90° can be used as a criteria for distinguishing between hydrophobic and hydrophilic surfaces. The surface characteristics are considered to be hydrophobic if the contact angle is greater than 90° .

The contact angle of Module 1 after a sequence of CO_2 absorptions is shown in Table 5.2.

Table 5.2 The contact angles of Module 1 after CO_2 absorption experiments

Sintering temperature ($^\circ$)	Grafting time (hour)	Contact angle (degree)		
		Original	Grafted fibre (with alkaline pre-treatment pH=11 for 8 hours)	After CO_2 absorption experiment
1300	8	64.55	134.35	129.63

The hydrophobic YSZ membrane was prepared via an improved surface modification technology. The contact angle of the grafted YSZ membrane was about 134° . After sequent absorption experiments which involved absorptions at high temperature (up to 333K) and with a high concentration of absorbent ($[\text{MEA}] = 7\text{M}$), the grafted YSZ membrane still maintained its hydrophobic character and the contact angle was around 130° . Most polymeric membranes do not maintain their hydrophobicity after contact with aqueous absorbent. The contact angles of the PE and the polytetrafluoro ethylene (PTFE) membrane were observed to be approximately 85° and 100° respectively by Nishikawa et al. [30] The observation implies that the polymeric membranes have become less hydrophobic which could result in a flooding problem during the absorption process. Compared to the polymeric membranes, the grafted ceramic hollow-fibre membrane showed a stable hydrophobicity.

5.5 Conclusion

In this study, hydrophobic ceramic hollow-fibre membranes have been successfully applied to CO_2 absorption by using an aqueous absorbent. The HTU of the membrane module was smaller than conventional packed columns by approximately one order of

magnitude. The performance of the membrane module showed a competent performance at high operating temperatures by using a higher concentration of absorbent which would wet or corrode most polymeric membranes. The stable hydrophobicity of the membrane module has also been demonstrated by contact angle measurements. The YSZ hollow-fibre membranes with thermal, chemical and hydrophobic stability are a promising possibility for application as a membrane contactor for CO₂ removal.

5.6 Notation

A: Area, m²

a: gas-liquid interfacial area per unit volume, m² m⁻³

C_A: concentration of gas A in the liquid phase, mol m⁻³

C_{Ae}: equilibrium concentration of gas A in gas and liquid phase, mol m⁻³

C_{Ai}: concentration of gas A at interface, mol m⁻³

C_{CO₂,i}: concentration of CO₂ at the gas-liquid interface, mol m⁻³

C_{CO₂,in}: CO₂ concentrations in the gas phase at the inlet, mol m⁻³

C_{CO₂,L}: concentration in the liquid phase, mol m⁻³

C_{MEA}: bulk concentration of MEA, mol m⁻³

C_{CO₂,out}: CO₂ concentrations in the gas phase at the outlet, mol m⁻³

d_c: hydraulic diameter, 4×(flow area/ wetted perimeter), m

d_i, d_o, d_p: inside, outside and log mean pore diameters of the hollow fibre, m

D_{g,b}: bulk CO₂ diffusion coefficient in the gas phase, m² s⁻¹

D_{g,L}: diffusion coefficient of CO₂ in the liquid phase, m² s⁻¹

D_{g,p}: effective CO₂ diffusion coefficient in the membrane pores, m² s⁻¹

D_k: Knudsen diffusion coefficient of CO₂, m² s⁻¹

D_{MEA,water}: diffusivity of MEA in water, m² s⁻¹

D_{CO₂,MEA}: diffusivity of CO₂ in MEA solution, m² s⁻¹

E: enhancement factor

H: Henry's law constant

HTU: height of transfer units, m

k_g, k_L, k_m: individual mass transfer coefficients in the gas, liquid, and membrane phases, m s⁻¹

K: overall mass transfer coefficient for CO₂, m s⁻¹

ℓ : length of hollow-fibre membrane, m
 L_p : effective pore length, m
 M : molecular weight of the gas, kg kmol⁻¹
 n : reaction stoichiometry
 n' : number of fibres
 NTU : number of transfer units
 N : mass transfer flux, mol m⁻² s⁻¹
 P : pressure, atm
 P_{CO_2} : partial pressure of CO₂ at the gas-liquid interface, kPa
 Pe : Peclet number
 Q_g : gas flow rate, m³ s⁻¹
 R : is the gas constant, J mol⁻¹ K⁻¹
 R_{CO_2} : absorption rate of CO₂, mol m⁻² s⁻¹
 Re : Reynolds number
 Sc : Schmidt number
 Sh : Sherwood number
 T : operating temperature, K
 T_0 : reference temperature, 298K
 V : molar gas flow rate, mol s⁻¹
 y : mole fraction of CO₂ in the gas phase
 y^* : equilibrium mole fraction of gas
 y_t : gas mole fractions at the top of the column
 y_0 : gas mole fractions at the bottom of the column
 z : length measured from the bottom of the column, m

Greek letters

ϵ_p : effective porosity
 μ : viscosity, Pa s
 v_g : superficial velocity, m s⁻¹
 ρ : density, kg m⁻³
 $\sigma_{g,b}$: Lennard-Jones parameter, Å
 $\Omega_{Dg,b}$: diffusion collision integral

Subscript

A: carbon dioxide
b: nitrogen
g: gas phase
in: inlet
L: liquid phase
M: membrane phase
out: outlet
p: membrane pore

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Chapter 6 Yttria-stabilized zirconia (YSZ)-based hollow fibre solid oxide fuel cells

Abstract

Electrochemical reactors such as solid oxide fuel cells (SOFCs) are highly efficient in converting chemical fuels to electrical power. Yttria-stabilized zirconia (YSZ) is one of the most popular electrolytes because of the low cost and its stability in the redox environment. In this study, asymmetric YSZ hollow-fibre membranes have been prepared at relatively lower sintering temperatures and shorter sintering durations using a combined phase inversion and sintering method. The produced YSZ hollow-fibre membranes with an asymmetric structure have shown a high mechanical strength of 296.7 MPa and a gastight property, which is essential for electrolyte applications. The inner porous structure of the YSZ hollow-fibre membranes provides good enhancement in nickel coating, resulting in the low resistance between the electrode (nickel) and the electrolyte (YSZ).

6.1. Introduction

Solid oxide fuel cells (SOFCs) have received considerable attention in recent years due to their high efficiency in converting chemical fuels to electrical power and lower emissions of SO_x , NO_x , CO_2 , and residual hydrocarbons compared to conventional combustion processes. The configurations in SOFCs can be classified into two types: (1) external-supporting and (2) self-supporting. The external-supporting SOFCs offer thinner cell components, but interconnected materials and high-temperature seals must be stable during thermal cycling. Compared with the external-supporting SOFCs, the self-supporting design can offer better thermal cycling capability and cheaper assembling costs.

In yttria-stabilized zirconia (YSZ)-based solid oxide fuel cells, the anode (nickel or platinum), cathode (lanthanum manganite or perovskite ceramics), electrolyte (YSZ), and external circuit are the essential components. In these components, the mechanical strength of the YSZ electrolyte is higher than anode and cathode materials

by approximately 1 order of magnitude and it is also cheaper. [1] Thus, it is the obvious choice for a self-supporting system. In addition, the YSZ is stable in the redox environment and also exhibits rapid ion diffusion across a wide range of temperatures (between 500 and 1000 °C) and oxygen partial pressures.

So far, two of the most common designs for electrolyte-supported cells are planar and tubular. The typical thickness for the electrolyte-supported SOFC made from the YSZ flat sheet is over 700 μm , [2, 3] whereas for the tubular configuration, the thickness is reported to be between 200 and 600 μm . [4, 5] These relatively strong supports from the electrolyte have higher ionic resistances because the ionic resistance of the electrolyte increases with the thickness. Recently, ceramic hollow-fibre membranes have received considerable attention not only because of the high mechanical strength and structural stability without any supports but also because of the comparatively large surface-to-volume ratio, which provides a potential for enhancing the solid oxide electrolyte utility for a given sized unit.

YSZ hollow-fibre membranes prepared by a combined phase inversion and the sintering method have been reported previously [6, 7] where the dense layer thickness of the membrane is approximately around 120 μm . However, the electrochemical performance has not been demonstrated. To use the YSZ hollow fibre as a solid oxide electrolyte for electrical power production, the gastight property of the fibre is essential, that is, the YSZ hollow fibre must be impermeable to both oxidant and fuel gases at both room and operating temperatures. By sintering YSZ precursors at around 1600 °C for 10 h, a dense and gastight structure of YSZ membranes has been demonstrated. [6, 8] However, long sintering time and high sintering temperature increase the electrolyte resistance as well as the production cost, making the electrolyte more difficult to commercialize.

This chapter aims at fabricating a thinner YSZ hollow fibre electrolyte-supported membrane with better mechanical strength and gastight properties. The membrane shows an asymmetric structure with a porous inner surface and a thin dense layer near the outer wall. The thin outer dense electrolyte layer minimizes electrolyte ohmic loss in SOFC operation, whereas the porous inner layer provides a higher surface area for

the anode electrode to be deposited. The proof-of-concept in preparing hollow fibre SOFCs has been demonstrated in this study.

6.2 Experimental

6.2.1 Materials

Commercially available 8 mol % yttria-stabilized zirconia (8 YSZ) powders with a particle diameter of 0.25 μm ($d_{50} = 0.25 \mu\text{m}$) (surface area 8-13 $\text{m}^2 \text{g}^{-1}$) purchased from NexTech Materials Ltd. (Ohio) were used for the preparation of the electrolyte membranes. Polyethersulfone (PESf) (Radel A300, Ameco Performance, USA) and 1-methyl- 2-pyrrolidinone (NMP) (HPLC grade, Sigma-Aldrich) and Solspers 3000 (provided by Noveon Inc., Ohio) were used as the binder, the solvent, and the additive, respectively. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\alpha}$ (LSCF) with a particle diameter of 0.6 μm ($d_{50} = 0.6 \mu\text{m}$) purchased from PI-KEM Ltd. (UK) was used as cathode material, whereas the nickel coating solution for preparation of the anode was supplied from Cookson Group plc.

6.2.2 Preparation of YSZ-based hollow fibre solid oxide fuel cells (SOFCs)

The immersion-induced phase inversion and sintering technique were employed in preparing the YSZ hollow-fibre electrolyte membranes. The detailed procedures were described elsewhere. [9] A spinneret with an orifice-diameter/inner diameter of 3.0/1.2 mm was used to obtain the hollow-fibre precursors. The parameters for preparation of the YSZ hollow-fibre precursors were summarized in Table 6.1.

Table 6.1 Spinning conditions of the YSZ hollow-fibre electrolyte membrane precursors

Parameters	Value
Compositions of the starting suspension (wt%)	
YSZ powder	68%
PESf	6.8%
Additive	0.12%
NMP	25.08%
Internal coagulant	5 vol.% NMP in DI water
External coagulant	Tap water
Spinneret dimension	
I.D./O.D.	1.2 mm/3.0 mm
Temperature	22 °C
Relative humidity	34%
Air gap	100 mm

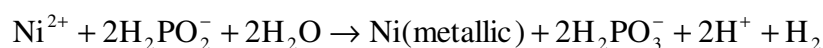
The final YSZ hollow-fibre electrolyte membranes were produced by heat treatment of the precursors in a CARBOLITE furnace with air. The furnace temperature was first increased at a rate of 3 °C min⁻¹ to 800 °C where the thermolysis (i.e., removal of the polymer binder) was carried out for 2 h. The temperature was then further increased to 1300-1500 °C at 5 °C min⁻¹ and was held there for duration of 3 h for final sintering. [9] Finally, cooling was carried out to room temperature at a rate of 5 °C min⁻¹.

After the YSZ electrolyte hollow-fibre membrane was produced, the cathode was deposited on the outer surface of the electrolyte membrane using the cathode material of La_{0.6} Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-α} (LSCF) and YSZ by a dip-coating method. The compositions of the dip-coating suspension are given in Table 6.2.

Table 6.2 Compositions of the cathode suspension

Chemicals	Weight %
YSZ (D ₅₀ = 0.25µm)	31.5%
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-α} (D ₅₀ = 0.6µm)	31.5%
1-methyl-2-pyrrolidinone (NMP)	29.88%
Polyethersulfone (PESf)	7%
Additive (Solsperse 3000)	0.12%

Before carrying out the coating, the ends of the YSZ hollow-fibre electrolyte membrane with 1.3 mm in diameter and 30 cm in length were sealed by epoxy resin (UK epoxyresins). Acetone was first used to degrease the outside surface of the YSZ hollow-fibre electrolyte membranes. After drying in air, the electrolyte membrane was immersed in the cathode dip suspension and then gradually removed from the suspension. The coated YSZ hollow-fibre electrolyte membrane was then dried and finally sintered at 1200 °C for 6 h with the same sintering profile as the YSZ hollow-fibre electrolyte membrane. The anode was deposited from a nickel hypophosphite solution (enplate 426) at 70 °C, whereas the nickel coating on the YSZ electrolyte support is based on the following chemical reaction:



A detailed mechanism of electroless nickel plating in hypophosphite solution was investigated by Honma and Kanemitsu [10] and Xu et al. [11] As the YSZ membrane is relatively inert and cannot be directly catalyzed by electroless nickel plating in hypophosphite solution, it was necessary to activate the YSZ support before plating. Tin chloride solution was used as a sensitizer and an acidic palladium chloride solution was used as an activator on the YSZ inner surface. Efforts were placed on optimizing the effective thickness of the anode coating to have an adequate axial conductivity, while not blocking anode/electrolyte/gas contact areas. This was performed by carefully controlling the deposition time, solution composition, temperature, etc. The detailed electroless plating procedures is given in Table 6.3.

Table 6.3 Process and compositions of activation and electroless nickel plating

Step	Process	Chemicals	Concentration	Time
1	Rinsing	n-Hexane	>99.0%	5 min
2	Sensitizing	SnCl ₂ ·2H ₂ O	1000 ppm	5 min
		HCl	1000 ppm	
3	Washing	DI water		–
4	Activating	Pd(NH) ₄ Cl ₄	1000 ppm	5 min
		HCl	1000 ppm	
5	Washing	DI water		–
6	Repeating step 2 to 5 for 3 times			
7	Drying in oven at 100 °C			Overnight
8	Electroless Ni plating at	Enplate 426A	100m L ⁻¹	10-15 min
	pH 6 and 70 °C	Enplate 426B	100ml L ⁻¹	
9	Washing	DI water		–
10	Drying in oven at 100 °C			Overnight

6.2.3 Characterization of hollow-fibre SOFCs

The mechanical strength of YSZ hollow-fibre electrolyte membrane was examined through a set of three-point bending tests using an Instron Model 5544 tensile tester with a load cell for 1 kN. Hollow fibres were fixed on the sample holder at 30 mm distance. The equation for the bending strength (σ_F) calculation is shown below: [12]

$$\sigma_F = \frac{8FLD}{\pi(D^4 - d_i^4)}$$

where F is the measured force at which the fracture occurred and L, D, and d_i are the length (30 mm), the outside diameter, and the inside diameter of the hollow fibres, respectively.

Scanning electron microscopy (SEM, JEOL JSM-5610LV, Japan) coupled with energy dispersive X-ray (EDX) analysis was used to study the morphologies of the YSZ electrolyte membrane, the LSCF cathode, and the nickel anode. Gastight

properties of the electrolyte membranes were measured using a method developed by Tan et al. [13] The details of the permeation calculation and the experimental setups are described elsewhere. [13, 14]

Current was collected from a digital multimeter (KEITHLEY, Model 195) by changing an adjustable resistance (Vishay, Model 534), while voltage was obtained from a voltage multimeter (ISO-Tech, IDM91E). During the testing, the cathode (LSCF + YSZ) was exposed to air and fuel (H_2) was supplied to anode (nickel). The test temperature was in a range between 600 and 800 °C.

6.3 Results and discussion

6.3.1 Morphology of YSZ hollow-fibre electrolyte membranes.

In this study, YSZ hollow-fibre electrolyte membranes consisting of an asymmetric structure with a porous inner surface and an outer dense thin layer have been prepared. To achieve such geometry, control of suspension composition and spinning parameters is considered to be important. It has been reported that air gap, internal coagulant, and humidity are the main factors affecting fibre geometries of polymeric membranes. [15-19] However, for ceramic membrane fabrication, the above factors were found to be less important. [7] Therefore, in this study, the asymmetric structure of the YSZ membrane was achieved using the spinning conditions given by Liu et al. [6, 7] with considerable modifications in sintering conditions. Figure 6.1 shows the morphologies of YSZ membrane precursors and YSZ electrolyte membranes sintered at 1400 °C.

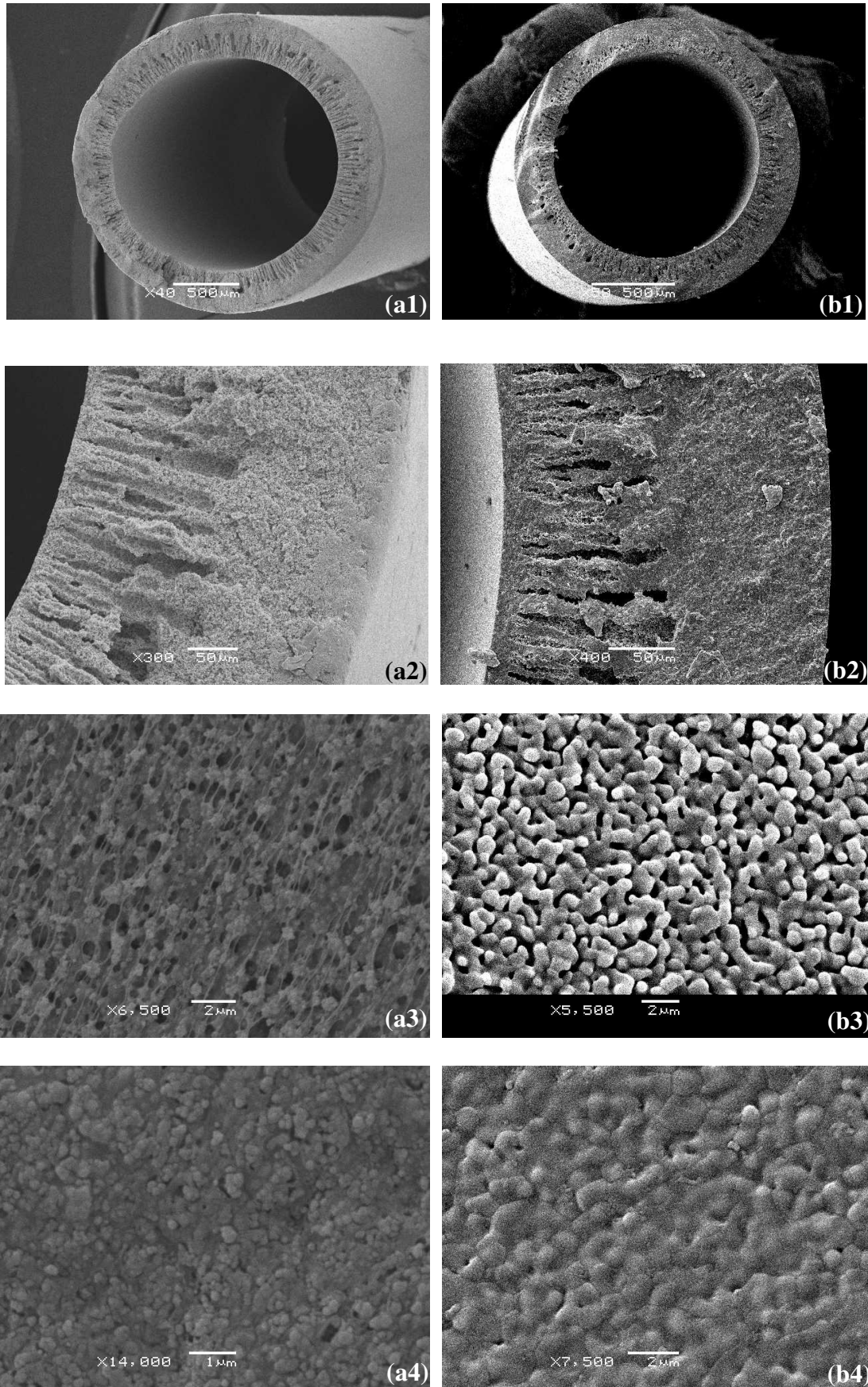


Figure 6.1 SEM images of YSZ electrolyte membrane, (a): precursor; (b): sintered membrane; (1): overall view of hollow fibre; (2): cross section of hollow fibre; (3): inner surface of hollow fibre; (4): outer surface of hollow fibre

The o.d./i.d. of the YSZ membrane precursors was about 2.38/1.67mm, as measured from part a1 in Figure 6.1. After sintering, the corresponding o.d./i.d. of the YSZ electrolyte membrane was shrunk to 1.28/1.17 mm, as shown in part b1 of Figure 6.1. The shrinkage of the YSZ membranes is due to the removal of polymer binder and solvent, and the rearrangement of the YSZ particles during the sintering.

The cross-sectional structure of the YSZ membrane precursor can be observed in parts a1 and a2 of Figure 6.1. It can be seen that a fingerlike structure was developed near the inner surface of YSZ membrane precursor, and a spongelike structure was formed near the outer surface. In general, a fast precipitation process causes a longer fingerlike structure, while a delayed precipitation process results in a spongelike structure. [20] It should be noted that to form a uniform and round YSZ hollow-fibre precursor, the NMP was found to be necessary to add into the internal coagulant. However, the presence of the NMP in the internal coagulant delays the precipitation rate resulting in elimination of the fingerlike structure near the inner surface. [20] To avoid this, a low NMP content solution (5 vol % NMP in water) was used for the internal coagulant to avoid the complete elimination of the fingerlike structure. Parts a3 and a4 of Figure 6.1 illustrate the inner and outer surfaces of the YSZ membrane precursor. It can be seen that the inner surface is much more porous than the outer surface and the YSZ particles are well dispersed and sparsely connected to each other by the polymer binder.

Parts b1-4 of Figure 6.1 depict the morphologies of the sintered membrane. It can be seen that the dimensions and the amount of the fingerlike pores became smaller and less respectively after sintering as shown in parts b1 and b2 of Figure 6.1. However, the special asymmetric structure, that is, the inner porous surface and outer dense surface, is retained as shown in parts b3 and b4 of Figure 6.1. The pore size of the inner surface is roughly 1 μm , whereas the outer surface is much denser. No obvious gas permeation can be detected using the gas permeation method developed by Kong and Li. [21] It seems that the spongelike structure is completely densified after the sintering, giving an overall thickness of the dense layer around 120 μm (part b2 of Figure 6.1).

6.3.2. Properties of YSZ hollow-fibre electrolyte membranes

Gas leakage in electrolyte membranes is often considered as a negative effect in SOFCs. The electrolyte membrane must be impermeable to both oxidant and fuel gases at both room and operating temperatures. As indicated by Nguyen, [22] the electrolytes of SOFCs are normally exposed to an extended oxygen partial pressure range from 10^{-18} to 10^2 kPa during operation. Therefore, in the study, the gastight property of the electrolyte membranes was measured at a starting pressure of 255 kPa. Figure 6.2 demonstrated a typical gastight result of YSZ hollow-fibre membranes where the pressure in the test module was plotted against the time.

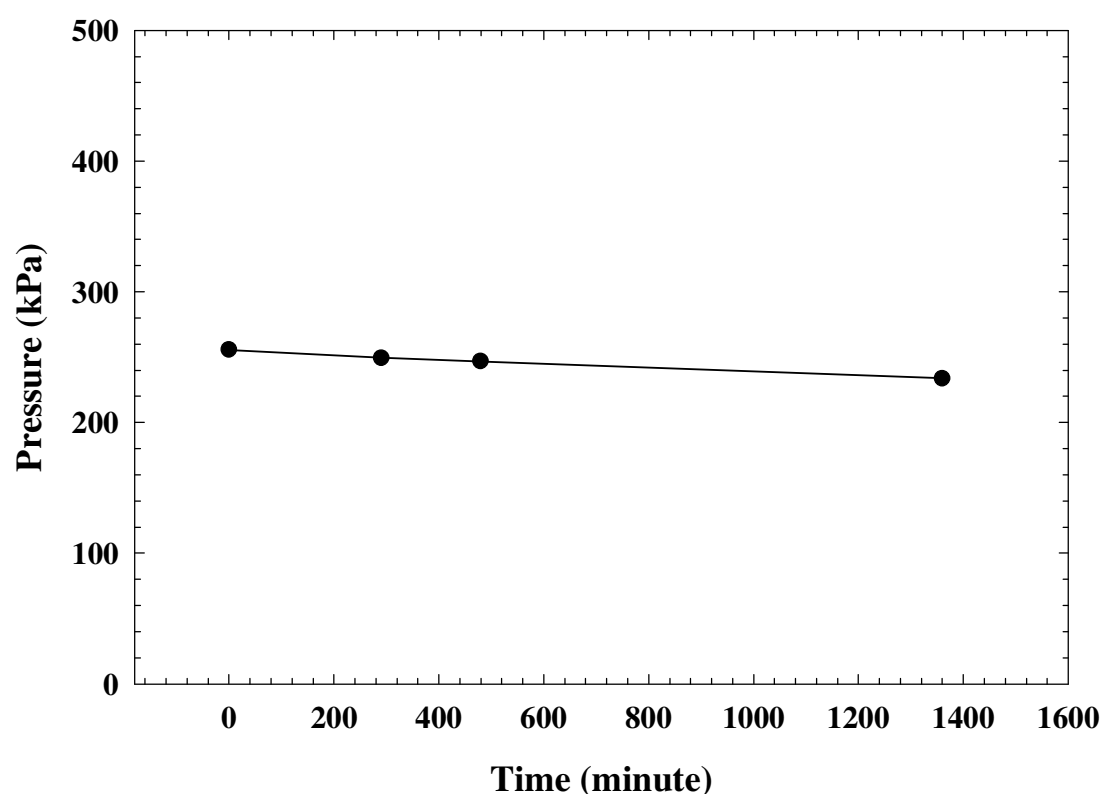


Figure 6.2 Gastight measurements of pressure vs testing time for a YSZ hollow-fibre membrane prepared at a sintering temperature of 1400 °C and for a duration of 3 h

The slight pressure decreases in the test module may be due to the trifling gas permeations through the membrane as well as possible leakages from joints of the system. Kim et al. [23] illustrated that the acceptable gas permeation of YSZ electrolyte is in the range of 1.7×10^{-9} to 5×10^{-8} ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$), which tested

below 2 bar. The gas permeation of the YSZ electrolyte membrane developed in this study is 3.2×10^{-10} ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) which is much lower than the acceptable values suggested by Kim et al. [23] It should be noted that the value of 3.2×10^{-10} ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) was calculated based on the results in Figure 6.2 using the equation given by Tan et al. [13]

Apart from the gastight property of the electrolyte membrane, mechanical strength is another important parameter, which must be determined. In this study, the mechanical strength of the YSZ electrolyte membrane was measured by the three-point bending tests at different sintering temperatures, and results are shown in Figure 6.3.

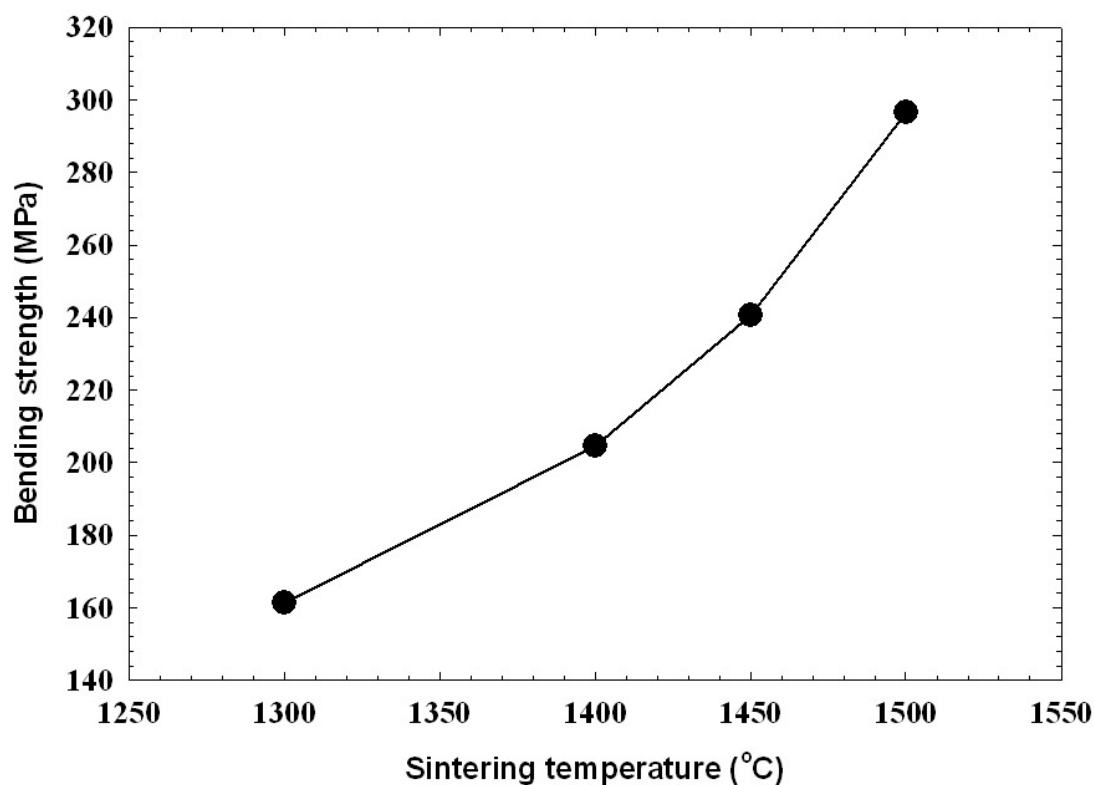


Figure 6.3 Effect of the sintering temperature on the mechanical strengths of the YSZ hollow-fibre membranes, sintering time 3 h

It can be seen that the mechanical strength of the membrane increased from 161 to 297 MPa as the sintering temperature is increased from 1300 to 1500 °C. It is obvious that as the sintering temperature increases the porosity of the YSZ membrane is reduced and the membrane is densified, offering higher mechanical strength.

Compared with the Al_2O_3 hollow-fibre membranes prepared with a similar particle size and sintering conditions, the mechanical strength of YSZ hollow-fibre membranes is about 6 times higher. [9] This high mechanical strength is beneficial in applying the membrane in practical use.

Figure 6.4 illustrates the XRD patterns of the YSZ electrolyte material and the YSZ electrolyte membrane.

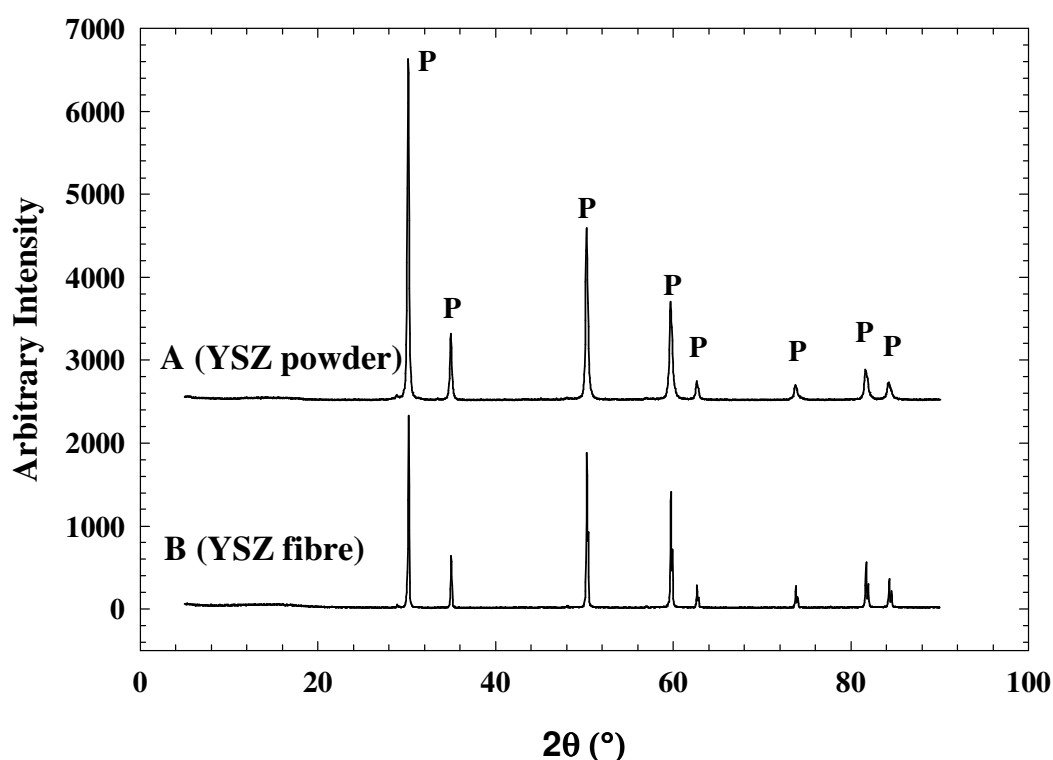


Figure 6.4 XRD patterns of the YSZ powder and YSZ hollow-fibre membrane

Peaks corresponding to the YSZ fluorite phase can be clearly observed and are in agreement with previously reported results. [24] It indicated that the YSZ electrolyte membrane remained in the same structure as the YSZ powder, although the grain size of the YSZ membrane is slightly bigger than the YSZ powders.

6.3.3 Coating of electrodes

Anode conductivity is very important for SOFC performance because the conductivity can minimize ohmic loss of SOFC. [25, 26] Nickel is a typical anode material of

SOFC due to its low cost, catalysis, and toughness. However, the adhesion between nickel and YSZ electrolyte is very poor for traditional flat sheet or tubular SOFCs. [27] In this study, a porous structure near the inner wall of the YSZ electrolyte membrane was prepared to improve the adhesion. As shown in Figure 6.1, the asymmetric YSZ hollow-fibre electrolyte membrane consists of a porous inner surface and a dense outer surface. The greater inner surface areas not only offer more than three phase boundaries for the oxidation between the anode and the electrolyte but also improve the adhesion between the anode and the electrolyte. Figure 6.5 shows the nickel distribution in the YSZ electrolyte membrane.

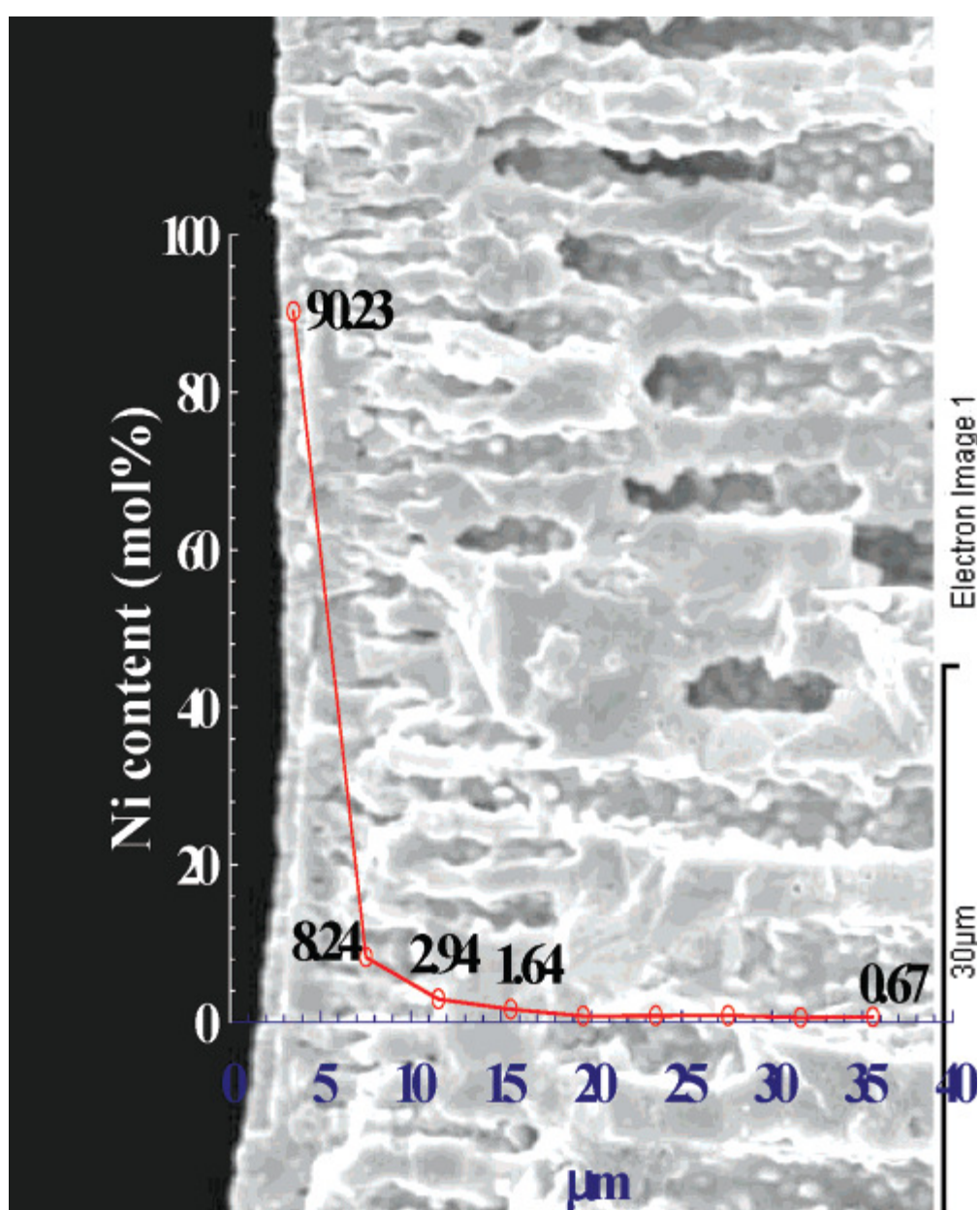


Figure 6.5 Energy dispersive X-ray (EDX) analysis of nickel content

From the EDX analysis, it can be seen that the nickel concentration decreased from the inner surface to the YSZ matrix, which indicates that nickel was deposited into the YSZ electrolyte membrane quite effectively.

As for the cathode development, LSCF has been selected as a cathode material of SOFC because of its high electrical conductivity in an oxidation atmosphere and acceptable compatibility with YSZ. [3, 28] In this study, a composite cathode of LSCF and YSZ with a half-weight ratio of the two components was prepared. This mixed electronic and ionic conductive cathode can provide additional reaction sites, which can decrease cathode polarization resistance. [29] The porous structure of the cathode can be seen from Figure 6.6. As a result of the porous structure, gas can diffuse to reaction sites and enhance the cathode performance.

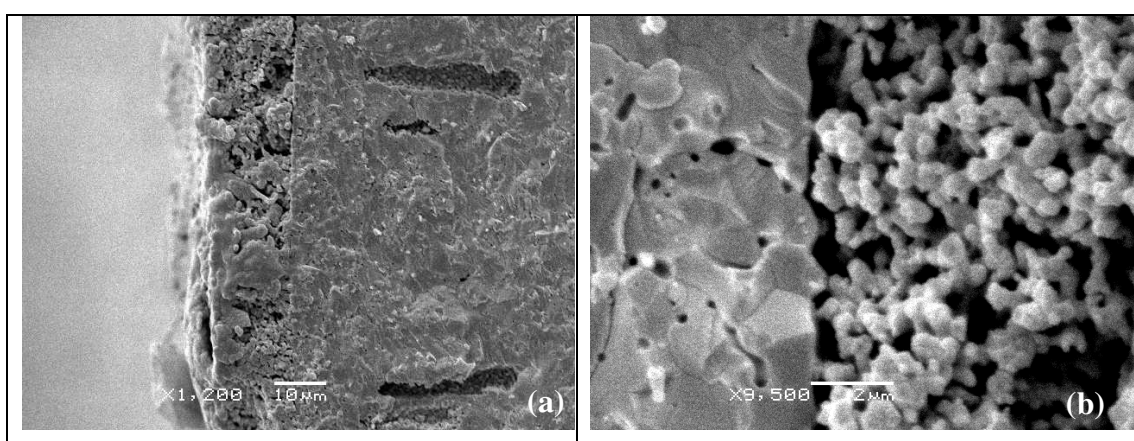


Figure 6.6 (a) Image of the LSCF/YSZ composite cathode prepared by the dip-coating method, (b) microstructure of the LSCF/YSZ cathode

Figure 6.7 shows an SEM image and an overall picture of YSZ hollow-fibre SOFC. It can be seen that the thickness and outer diameter of the hollow-fibre SOFC are about 269 and 1580 μm, respectively.

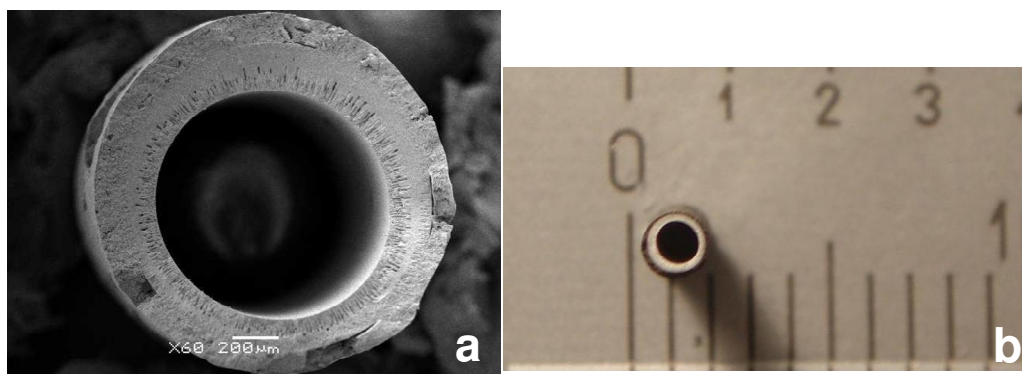


Figure 6.7 Overall views of (a) SEM image of hollow-fibre SOFC, (b) digital picture of hollow-fibre SOFC

6.3.4 Electrochemical performance

To evaluate the performance of the hollow-fibre SOFC, an electrochemical test was performed on the cell (LSCF+YSZ)/YSZ/nickel with air as an oxidant and 100% H_2 as a fuel at 600 to 800 °C. The results are shown in Figure 6.8.

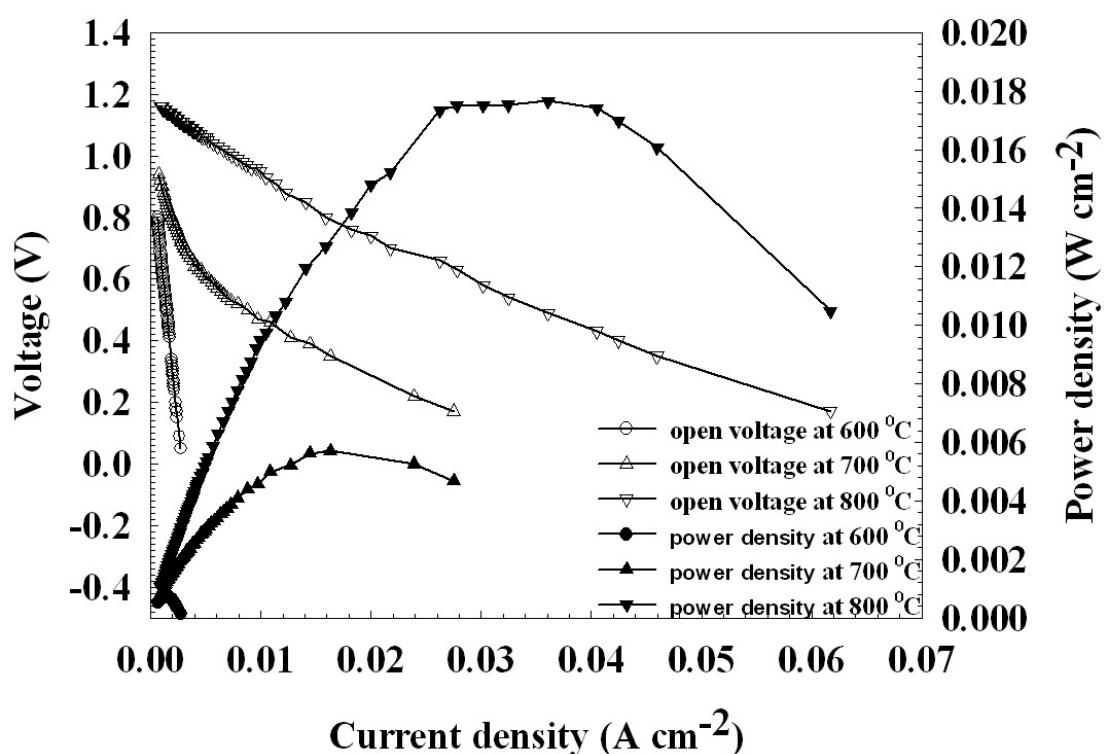


Figure 6.8 Performance of a hollow-fibre solid oxide fuel cell showing voltage and power density as a function of current density and temperature. The cell consisted of air, (LSCF+YSZ)/YSZ/Ni, and H_2 at a constant gas flow rate of $20\ cm^3\ min^{-1}$

In most tests, the power densities/current densities relation tends to be parabolic, but they take different time to reach the maximum value. The maximum power density in this study was about 0.018 W cm^{-2} at 800°C with an effective operating length of 4 cm (constant temperature zone of the furnace). The power densities of electrolyte-supported SOFCs are relatively lower than other types of supported SOFCs. Although the thicker electrolyte would provide good mechanical strength, one of the disadvantages of the electrolyte-supported SOFCs is the higher electrolyte ohmic loss, which causes a lower power density. Therefore, it is important to minimize the thickness of the electrolyte, and at the same time, to maintain sufficient mechanical strength. Apart from minimizing the ohmic loss, Hatchwell et al. demonstrated that improvement of the interconnection between the electrode and electrolyte could also enhance power densities. [30] It is, therefore, envisaged that the power density can be considerably improved once the structure of the electrolyte support is optimally designed.

It is also noticed that a high and stable open voltage (near 1.2 V) was obtained in the test, which indicated a good gas tightness of the YSZ electrolyte support. [31] At high operating temperature, the cell voltage curve decreased slower than those operated at a low operating temperature. This phenomenon resulted from YSZ, which has a better ionic conductivity at high temperature. [32]

6.4 Conclusions

A hollow-fibre SOFC based on the YSZ electrolyte membrane has been successfully prepared in this study. The porous inner surface showed a higher surface area for nickel loading, and the dense layer at the outer wall provided good ionic conductivity. The YSZ hollow-fibre electrolyte membrane showed good mechanical strength and excellent gastight properties. After coating with a cathode (LSCF/YSZ) and an anode (nickel), the hollow-fibre SOFC demonstrated its electrochemical performance. The concept of YSZ hollow-fibre SOFC has been successfully proven in this study. As a result of high packing densities in hollow-fibre configuration, these YSZ hollow-fibre SOFCs have a high potential for practical applications.

6.5 References

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Chapter 7 Conclusions

This thesis focuses on the fabrication and application of yttria stabilized zirconia (YSZ) hollow-fibre membranes which have superior thermal and chemical stability compared to polymeric membranes as well as greater mechanical strength, compared to most other ceramic membranes. Asymmetric YSZ membranes were prepared in a single step by using an immersion induced phase inversion technique. Two different structures of YSZ membrane have been developed in this study; porous and non-porous structures. The porous YSZ membranes were then, after surface modifications, packed into stainless steel modules and have been used as a membrane contactor for CO₂ absorption. The non-porous membranes have been used as a solid electrolyte in solid oxide fuel cells. The major findings found in this study are summarized below.

7.1 Major findings

7.1.1 Ceramic asymmetric hollow-fibre membrane preparation

(a) Ceramic hollow-fibre membranes which have an asymmetric structure have been prepared in a single step by spinning a suspension containing the YSZ particles with distributed particle sizes, through a conventional tube in-orifice spinneret. It is believed that the asymmetric structure is formed because of viscous fingering and the different rates of particle movement during the phase inversion. The results shown in this study indicate that good control of the particle size distribution in the suspension and the exchange rates of the solvent and non-solvent may allow the asymmetric membrane structure to be tailored specifically, something which can only be achieved in multiple steps if conventional techniques are employed.

(b) Gas permeation analyses suggest that both porous and non-porous YSZ hollow-fibre membranes can be prepared depending on the sintering conditions. Non-porous YSZ hollow-fibre membranes were prepared at a sintering temperature of 1400 °C or greater, below which the membrane contains pores. Pore sizes of the YSZ porous membrane were found to be in the ultrafiltration range. However, the surface porosities of the membranes prepared from suspensions with two particle size

populations at sintering temperatures of 1200 °C and 1400 °C are around 5000 m⁻¹ and 300 m⁻¹, respectively. The former is comparable to polymeric membranes, while the latter is an order of the magnitude smaller.

7.1.2 Fabrication of hydrophobic ceramic membrane

(a) A robust and hydrophobic YSZ hollow-fibre membrane was successfully developed in order to extend the use of porous ceramic hollow-fibre membranes to applications requiring hydrophobic membranes. An improved alkaline pretreatment step was introduced to the surface grafting method. After alkaline pre-treatment, the grafted YSZ hollow-fibre membranes showed a dynamic contact angle with water of up to 140°. The contact angle results show that hydroxyl groups have been efficiently restored on the ceramic membrane surface and have further enhanced the hydrophobicity of the ceramic membranes.

(b) The overall morphologies of the YSZ membranes were maintained after the surface grafting process and they showed high mechanical strength, which is important for practical applications. The grafted membranes also demonstrated thermal stability up to 270 °C and chemical stability in hexane.

7.1.3 CO₂ absorption by using hydrophobic YSZ membrane

(a) Hydrophobic YSZ membranes have been successfully applied to CO₂ absorption using an aqueous absorbent. The HTU of the membrane module was smaller than conventional packed columns by approximately one order of magnitude. The membrane module showed competent performance at high operating temperatures using a higher concentration of absorbent which would wet or corrode most polymeric membranes.

(b) The theoretical prediction was in agreement with the experimental value of K_g.

(c) The hydrophobicity of the membrane module was stable, as shown by their unchanged contact angle measurements with water. The YSZ hollow-fibre

membranes with thermal, chemical and hydrophobic stability have been shown to be a promising alternative for industrial scale applications.

7.1.4 YSZ based hollow-fibre solid oxide fuel cell

(a) For the first time, a non-porous YSZ hollow-fibre membrane has been successfully designed for a solid oxide fuel cell (SOFC) application. A ceramic hollow-fibre SOFC based on an asymmetric YSZ electrolyte membrane has been prepared in this study. The porous inner surface offered a high surface area for nickel loading, and the dense layer at the outer wall provided good ionic conductivity.

(b) The YSZ hollow-fibre electrolyte membrane exhibited good mechanical strength and excellent gastight properties. After coating with a cathode (LSCF/YSZ) and an anode (nickel), the electrochemical performance of the hollow-fibre SOFC was demonstrated.

7.2 Recommendations for future work

(a) Membrane morphology:

In this study, the asymmetric ceramic hollow-fibre membrane was successfully prepared by controlling the size of ceramic particles and the air gap. Nevertheless, other factors such as suspension viscosity, non-solvent additive and internal coagulant flow rate etc. can also affect the morphology of the ceramic hollow-fibre membrane. [1] Further studies on the effect of spinning conditions on the structure of YSZ hollow-fibre membranes are recommended.

(b) CO₂ capture study:

A few groups have been working on the development of ionic liquids to achieve CO₂ absorption at high temperature without cooling down flue gases. [2, 3] The combination of ionic liquids and membrane technology has only recently been applied to gas absorption. [4, 5] So far, only polymeric flat sheet membranes have been used in the process, limiting the process operation to lower temperatures. It is recommended that ceramic hollow-fibre membrane contactors should be applied to the process as the properties of ceramic hollow-fibre membrane contactors, such as

chemical and thermal stability as well as high surface area unit volume are all beneficial in CO₂ capture technology.

(c) Electrochemical performance of hollow-fibre SOFC:

The electrochemical performance of the developed hollow-fibre SOFC can still be improved for the commercial market. It is recommended that the thickness of electrolyte layer should be minimized in order to reduce the ohmic loss. To achieve this, the anode (nickel) could be deposited as close as possible to the underlying dense layer of electrolyte. In order to allow for deeper nickel deposition, bigger pore entrances on the inner surface should be designed.

(d) Production cost:

The production costs of ceramic membranes are still not competitive when compared to those of polymeric membranes due to the energy-consuming sintering processes involved in most ceramic membrane fabrication. Therefore, their commercial value is focused on the niche markets in which polymeric membranes cannot be used. Therefore, employment of ceramic membranes in areas such as solvent separation, gas separation at high temperature and other applications involving membrane contactors such as solvent distillation and gas stripping processes is recommended.

7.3 References

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List of Publications

1. Chiao Chien WEI and K. Li., Preparation and Characterization of a Robust and Hydrophobic Ceramic Membrane via an Improved Surface Grafting Technique, *Ind. Eng. Chem. Res.* **2009**, 48, 3446.
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